



Helmholtz-Zentrum für Ozeanforschung Kiel

## **RV SONNE**

### **Fahrtbericht / Cruise Report**

### **SO218 SHIVA**

**Stratospheric Ozone: Halogens in a Varying Atmosphere**

Part 1: SO218- SHIVA Summary Report (in German)

Part 2: SO218- SHIVA English reports of participating groups

15.-29.11.2011

Singapore - Manila, Philippines



Berichte aus dem GEOMAR  
Helmholtz-Zentrum für Ozeanforschung Kiel

**Nr. 12 (N. Ser.)**

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# **RV SONNE - Cruise**

## **SO218- SHIVA**

Singapore to Manila, Philippines

15 to 29 November 2011

(In the frame work of the SHIVA Western Pacific campaign in November and December 2011.)

Part 1: SO218- SHIVA Deutscher Übersichtsreport

Part 2: SO218- SHIVA English reports of participating groups

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**Teil 1: SO218- SHIVA Deutscher Übersichtsreport****SO218-SHIVA: Stratosphärisches Ozon: Halogen Einfluss in einer sich verändernden Atmosphäre**

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## **SO218-SHIVA: STRATOSPHERISCHES OZON: HALOGEN EINFLUSS IN EINER SICH VERÄNDERNDEN ATMOSPHERE**

### **I.1. AUFGABENSTELLUNG**

Im Rahmen des EU-Projektes SHIVA (Stratospheric Ozone: Halogens in a varying atmosphere) sollten in Feldstudien kurzlebige Substanzen mit klimasensitiven natürlichen Emissionen untersucht werden, im Besonderen waren ozeanische leichtflüchtige Brom- und Jodverbindungen in tropischen Regionen, die als Hauptquellorte für die Stratosphäre gelten, ein Ziel der Forschung. SHIVA-„Stratospheric halogens in a varying atmosphere“ beinhaltet ein aktuelles Forschungsthema der „World Meteorological Organization“ (WMO) Ozonforschung und ist fest in internationalen Programmen verankert. Auf der Forschungsseereise SHIVA-Sonne im Südchinesischen Meer und in philippinischen Gewässern von Singapur bis Manila vom 15. bis zum 29. November 2011 wurden in interdisziplinärer Zusammenarbeit Produktion, Emission und Transport der Verbindungen in bisher nicht untersuchten Küstenregionen des West-Pazifik erforscht. Die Kampagne fand zu Beginn der tropischen Hauptkonvektionszeit in dem Haupteintragsort troposphärischer Luftmassen in die Stratosphäre statt, wo marine Quellen mit Bedeutung für die Ozonschicht untersucht wurden. Auf *FS Sonne* wurden das Meerwasser und die von ozeanischen Emissionen beeinflusste Luft analysiert. Mit dem deutschen Forschungsflugzeug Falcon, das zur gleichen Zeit auf Borneo (Miri, Malaysia) stationiert war, wurde versucht die gleichen Luftmassen wie auf *FS Sonne* zu analysieren. Anorganische Zersetzungsprodukte der Halogenverbindungen und der Spurengashaushalt der Atmosphäre wurden gemessen und die chemische Transformation der ozeanischen Emissionen vom Erdboden bis in die tropische Tropopausenschicht und ihr Eintrag in die Stratosphäre wurden modelliert. Die Messung biologischer, ozeanographischer und chemischer Parameter im Ozean mittels in-situ Messungen und Fernerkundungsmethoden in Zusammenarbeit mit malaysischen und philippinischen Kollegen wurden für Quellzuordnungen der marinen Spurengase herangezogen. Für küstennahe Untersuchung wurden Probenahmen mit lokalen Booten von ortsansässigen Universitäten organisiert, sowie ein zweimaliger Probenaustausch zwischen den Booten und *FS Sonne* durchgeführt.

### **I.2. VORHABEN**

Das EU- Projekt SHIVA (2009-2013), dessen zentraler Bestandteil die durchgeführte Forschungs-seereise SHIVA-Sonne war, beinhaltet einen aktuellen Forschungsschwerpunkt der Ozonforschung, der im letzten „Ozon-Bericht“ der WMO von 2011 hohe Priorität erhielt, wobei es um den Beitrag ozeanischer kurzlebiger Verbindungen zum stratosphärischen Brom und zur Ozonzerstörung geht. Dieser stratosphärische Bromeintrag wird aktuell weltweit mit etwa 5 ppt als Annahme in Klimachemiemodellen berücksichtigt, um den beobachteten Ozonabbau der mittleren Breiten simulieren zu können. Die Frage woher, wie schnell und in welchen Mengen dieses Brom in die Stratosphäre gelangt, ist bisher nicht geklärt. Vermutlich kommt dem Gebiet um den maritimen Kontinent im West Pazifik dabei die größte Bedeutung zu. In diesem Hauptkonvektionsgebiet finden im nordhemisphärischen Winter ca. 60 % aller globalen Einträge troposphärischer Luftmassen in die Stratosphäre statt.

Die Seereise wurde zur Ermittlung der Emissionen im tropischen küstennahen Westpazifik für den bisher keine ozeanischen Messungen kurzlebiger Bromverbindungen und anderer halogenierter Kohlenwasserstoffe existierten, und ihres Transportes durch die Troposphäre bis in die Stratosphäre durchgeführt. Die ozeanischen Konzentrationsverteilungen und Emissionen der halogenierten Verbindungen und weiterer klimarelevanter Spurengase (DMS, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>) sowie der Phytoplanktongehalt des Meerwassers wurden ebenfalls bestimmt. In malaysischen und philippinischen

Gewässern wurden einige CTD-Stationen durchgeführt, um die chemische und biologische Produktion der Spurengase im Ozean (Tiefenprofile) und deren Gehalte und Quellen im Oberflächenwasser besser zu verstehen.

Die Vor- und Nachbereitung der Seereise war aus diplomatischen und logistischen Gründen aufwändig und erforderte mehrere Besuche in Malaysia, sowie eine Fahrtplanung und -durchführung, die neben den wissenschaftlichen Fragestellungen, Ausschlussgebiete, Piratenaktivitäten, Territorialstreitigkeiten, Küstenfischerei, sowie schwierige Passagen wegen unklarer oder zu flacher Bathymetrie berücksichtigen musste. Die kombinierte internationale Messkampagne mit FS Sonne, zusätzlich einigen kleinen küstennahen Einsätzen von Forschungsbooten, dem deutschen Forschungsflugzeug Falcon, sowie gleichzeitige Messungen vom Erdboden und vom All aus, wie sie im Westpazifik im Herbst 2011 durchgeführt wurde, ist einmalig und sehr erfolgreich verlaufen.

### **I.3. PLANUNG UND ABLAUF DES VORHABENS**

Wissenschaftler aus 18 Einrichtungen in Europa und Asien erforschten im EU- Projekt SHIVA die natürlichen Ursachen für den stratosphärischen Ozonabbau, wobei das Helmholtz-Zentrum für Ozeanforschung Kiel (GEOMAR) die marinen Messungen der großen SHIVA-Kampagne im November 2011 koordinierte. Das Hauptarbeitsgebiet während der Seereise lag zwischen 0°/102°E und 14°N/120°E. Für das Forschungsgebiet wurde eine Route geplant, die den wissenschaftlichen Zielen entsprach und dabei nicht zu weit von der Borneo-Küste entfernt lag und nicht in chinesische, bzw. malaysisch-indonesische Gewässer vordrang. Die kontinuierliche Luft- und Meerwasserbeprobung fand in den Hoheitsgebieten Malaysias, Bruneis und der Philippinen statt. Über das Auswärtige Amt (Herr Mahrle) wurde am 10. Januar 2011 zusammen mit dem sogenannten EPU (Economic Planing Unit)-Proposal (verfasst vom SHIVA- Projektkoordinator Klaus Pfeilsticker) der diplomatische Antrag (Marine Scientific Research Application) an Malaysia eingereicht. Am 23. März 2011 wurde das Projekt im National Security Council von Malaysia beraten und grundsätzlich bewilligt. Am 10. Mai 2011 wurden die diplomatischen Anträge auf Meeresforschung an die deutschen Botschaften in Brunei und die Philippinen gesandt, die vor Antritt der Seereise bewilligt wurden. Die Flug-Hoheitsgebiete sind von denen der marinen EEZ sehr verschieden, und Anträge für Fluggenehmigungen wurden für das Flugzeug Falcon von der DLR an die jeweiligen Staaten gestellt. Vom 15. bis 29. November 2011 wurde die Expedition SO218 dann durchgeführt. Vom Starthafen Singapur aus operierte FS Sonne im Südchinesischen Meer und der Sulu See vor Malaysia, Brunei und den Philippinen und lief als Endhafen Manila (Philippinen) an. Das Schiff folgte einer Fahrtroute entlang der Schelfgewässer der West- und Nordküste Borneos, durch die tiefe Sulu See bis in Küstengewässer der Insel Luzon. Während der Fahrt wurden dreistündig Luft- und Wasserproben gewonnen, die während zweier Tagesstationen am 18. und 21. November auf stündlichen Rhythmus erhöht wurden. Es wurden zusätzlich an 14 Stationen ca. 40 Tiefenprofile mit der CTD und dem Kranzwasserschöpfer gefahren und mehr als 60 Radiosondierungen der Atmosphärenstruktur durchgeführt, sowie 6 Ozonsonden gestartet. So wurden atmosphärische und ozeanische Konzentrationen bromierter, jodierter und chlorierter Halogenkohlenwasserstoffe erhalten, um ihre marinen Emissionen berechnen zu können. Ebenso wurden physikalische Ozeanparameter, sowie Phytoplankton- und Zooplanktonspezies untersucht, um die Quellen der Verbindungen bestimmen zu können. Die ozeanischen Konzentrationen weiterer Spurengase wie Dimethylsulfid (DMS), Distickstoffoxid (N<sub>2</sub>O), Methan (CH<sub>4</sub>), Kohlendioxid (CO<sub>2</sub>) und Sauerstoff (O<sub>2</sub>) wurden gemessen, um ihre Herkunft und Quellstärken in dieser Region sowie ihre Korrelationen mit den Halogenkohlenwasserstoffen zu analysieren. Meteorologische Parameter, atmosphärisches Ozon, sowie reaktive Halogenabbauprodukte, ebenso wie weitere atmosphärische natürliche und anthropogene Spurengase, vornehmlich als Verschmutzungsindikatoren wurden zusätzlich bestimmt.

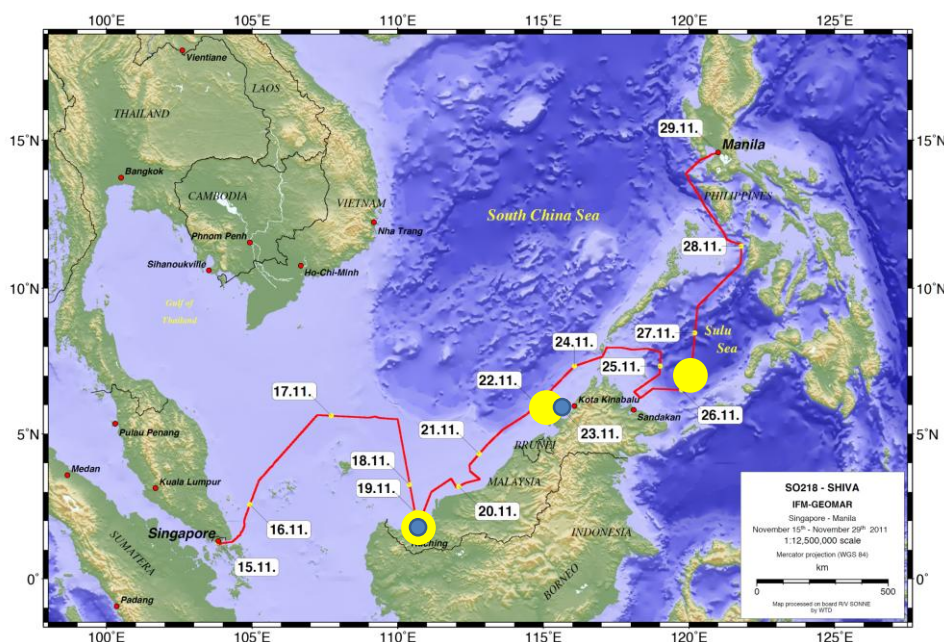


Abbildung 1: **SO218-FAHRTVERLAUF** FS Sonne Singapur-Manila (15.-29. November 2011) mit Bootskontakten und Küstenproben austausch (blaue Kreise) und Überflüge von Falcon (gelbe Kreise).

Das an Bord durchgeführte Arbeitsprogramm:

- Kontinuierliche Meerwasserbeprobung mit eigenem Pumpsystem im hydrographischen Schacht zur Messung von Spurengasen, sowie hydrographischen und biologischen Parametern im Oberflächenwasser.
- Sammlung diskreter Luftproben auf dem Peildeck.
- Aerosolfilterproben der Atmosphäre auf dem Peildeck.
- Atmosphärenchemische und optische Messungen durch mehrere Sensoren auf Peildeck. Ballonaufstiege vom Hauptdeck des Schiffes.
- Messungen der Luft- und Meerwasserproben mit Gaschromatographie/ Massenspektrometriesystem (GC/MS).
- Massenspektrometrische Messungen der Atmosphäre in einem Laborcontainer auf dem Vordeck des Schiffes.
- In situ-Messungen von Ozean-optischen Eigenschaften und Phytoplankton.
- 11 flache und drei tiefe Stationen für CTD- und Wasserprobennahme.
- Koordination mit Flugzeugmessungen, des zeitgleich auf Borneo stationierten Forschungsflugzeuges DLR Falcon.
- Koordination des Treffens und Proben austausches mit zwei küstennahen Booten.

Für eine übersichtlichere Darstellung der Arbeiten während der Seereise wurden die teilnehmenden Gruppen in 11 Arbeitsgruppen aufgeteilt:

	VW	Arbeitsgruppe	Teilnehmer	Teilnehmer	Funktion	Universität/ Institut	Methoden	
	Verantwortliche/r Wissenschaftler/in (VW)	Nummer und Bezeichnung	Nachname	Vorname	Funktion	Universität	Methoden und Daten	
	Schiff						meteorologische und ozeanographische Daten	
			Quack	Birgit	leitende Wissenschaftlerin	IFM-GEOMAR		
Beobachter Malaysia: Said Sapli, Beobachter Philippinen: Benjamin Z. Magura								
im Wasser	Quack	1a: Halogenierte Kohlenwasserstoffe (MS)	Hepach	Helmke	Studentin	IFM-GEOMAR	halogenierte Kohlenwasserstoffe in Wasser und Atmosphäre:  $\text{CH}_3\text{I}$ , $\text{CH}_2\text{Cl}_2$ , $\text{CHCl}_3$ , $\text{CCl}_4$ , $(\text{CH}_3\text{CCl}_3)$ , $\text{CH}_2\text{Br}_2$ , $(\text{C}_2\text{H}_5\text{CCl}_3)$ , $\text{CHBrCl}_2$ , $\text{CH}_2\text{ClI}$ , $\text{CH}_2\text{BrI}$ , $\text{C}_2\text{Cl}_6$ , $\text{CHBr}_2\text{Cl}$  $\text{CHBr}_3$ , $\text{CH}_2\text{I}_2$	
			Petrick	Gert	Techniker	IFM-GEOMAR		
			Qiang	Shi	Studentin	IFM-GEOMAR		
			1b: Halogenierte Kohlenwasserstoffe (ED)	Raimund	Stefan	Wissenschaftler	IFM-GEOMAR	$\text{CHBr}_3$ , $\text{CH}_2\text{I}_2$
	Bracher	2a: Biologie; Pigmente	Altenburg Sopha	Mariana	Wissenschaftlerin	AWI- BREMERHAVEN	Pigmente, Bestrahlungsstärke, Strahlung  Flowzytometrie, Chlorophyll-Fluoreszenz Mikroskopie; Fernerkundung	
			Wiegmann	Sonja	Technikerin	AWI- BREMERHAVEN		
			Cheah	Wee	Wissenschaftler	AWI- BREMERHAVEN		
	Malaysia	2b: Biologie	Idid	Rizman	Wissenschaftler	U Malaya Kuala Lumpur	Biologie / ADCP/PAM/ Zooplanktonzusammensetzung	
			Muhajid	Aazani	Wissenschaftlerin	UNIMAS Malaysia Sarawak	Biologie, (Satelliten-)fernerkundung, Molekularbiologie	
	Philippinen			Palermo	Joseph	Wissenschaftler	University of the Philippines Diliman	Biologie/Flow-Cam / , Phytoplanktonzusammensetzung,
	Marandino	3a: OVO, C	Zindler	Cathleen	Student/in	IFM-GEOMAR	OVOC: Aceton, Acetaldehyde, Propanal, Butanal, Butanon	
	Quack	3b: Ox, Nuts	Marandino	Christa	Studentin	IFM-GEOMAR	Nährstoffe und sauerstoff ( + Atmosphärenproben)	
		3c: $\text{N}_2\text{O}$ , $\text{CH}_4$ , DMS					ozeanische Spurengase ( $\text{N}_2\text{O}$ , $\text{CH}_4$ , DMS)	
	Körtzinger	4: $\text{P}_{\text{CO}_2}$ , $\text{P}_{\text{O}_2}$ , S.T	Müller	Christian	Student	IFM-GEOMAR	$\text{P}_{\text{CO}_2}$ / $\text{P}_{\text{O}_2}$ CTD (Temp., Sal.);FREON; Probenahmen Gasdruck: Druck aller Gase im Meerwasser, DIC, Alkalinität	
in Luft	Krüger	5: Radiosonde	Krüger	Kirstin	Wissenschaftler/in	IFM-GEOMAR	Schiff und Flugzeugkoordination, Radiosonde (60)  DISDROMETER, Regensensor ( Niederschlag, Tröpfchengröße)  $\text{CO}$ , Wasserdampf, $\text{O}_3$ Sonden (Cirruswolken, Feuchtigkeit)	
			Immler	Franz	Wissenschaftler/in	IFM-GEOMAR		
			Fuhlbrügge	Steffen	Student	IFM-GEOMAR		
	Atlas	6: Luftprobennahme	Witke	Franziska	Studentin	IFM-GEOMAR	> 50 atmosphärische Spurengase: halogenierte KWs, Alkane (200)	
							Zusammensetzung der Aerosole: Br, I, Nährstoffe, $\text{N}_2\text{O}$ , $\text{CH}_4$ ,	
	Pfeilsticker	7: CE- DOAS	Lampel	Johannes	Student	Uni Heidelberg	MAX DOAS: BRO, IO, Cavity ring down : IO	
	Harris/ Kreher	8: $\mu$ - DIRAC	Kinzel	Julian	Wissenschaftler/in	Cambridge/NiWA/ IFM-GEOMAR	$\mu$ -DIRAC: kontinuierliche atmosphärische halogenierte KWs	
	Schlager	9: $\text{CO}$ , $\text{CO}_2$ , $\text{CH}_4$ , $\text{O}_3$	Sentian	Justin	Wissenschaftler/in	University Malaysia Sabah	PICARRO: $\text{CH}_4$ , $\text{CO}_2$ , $\text{O}_3$ , CO	
			Abdullah	Nur Aleesha	Wissenschaftler/in	Malaysian meteorologische Abteilung		
		Voigt	10a: CIMS, Br	Jurkat	Tina	Studentin	DLR	CIMS: atmosphärische Spurengase Br, HBr, BrO
10b: IO, OH, Hox	Schäuble		Dominik	Wissenschaftler/in	DLR			
	Heard	10c: Containerinformation	Ingham	Trevor	Wissenschaftler/in	Uni Leeds	LIF: IO	
			Bunyan	Hannah	Studentin	Uni Leeds		
	Baker	11: Aerosole				UEA Norwich	Chlor , Brom und Iodgehalt von Aerosolen	

Tabelle 2: Arbeitsgruppeneinteilung auf SHIVA-Sonne (Singapur- Manila, November 2011).

FS Sonne kann wegen ihres Tiefgangs nicht sehr nah an Küstenlinien heranfahren (>20m Tiefe), zusätzlich behinderten Fischerei, Bohrtürme und Piraterie den Küsteneinsatz. In Küstennähe wurden zudem hohe Konzentrationen der kurzlebigen Verbindungen erwartet und besonders der Gradient zwischen küstennahen und offeneren Gewässern war für weitere Modellrechnungen von Interesse. Daher wurden von Wissenschaftlern der ortsansässigen Universitäten in Kuching (UNIMAS/ Sarawak, Dr. Lim Po Teen), in Kota-Kinabalu (UMS/Sabah, Prof. Dr. Ann Anton) und in Kuala-Lumpur (UM, Prof. Phang Sew Moi) für einige Küstenstellen lokale Bootseinsätze durchgeführt. Auf diesen Bootseinsätzen sollten die Wissenschaftler alle 5 km von der Küste entfernt Wasserproben nehmen, die dann bei einem kurzen Treffen zwischen FS Sonne und dem Universitätsboot ausgetauscht werden sollten. Im Gegenzug dazu sollten die ortsansässigen Wissenschaftlern Wasserproben von der offenen See erhalten. So wurden am 19. November 2011 innerhalb von zwei Stunden küstennahe Proben beim Treffen mit einem örtlichen Boot der Universität UNIMAS vor Kuching und am 22. November mit einem Boot der Universität UMS vor Kota Kinabalu ausgetauscht. Die vorher geplanten Besuche der malaysischen Wissenschaftler an Bord von FS Sonne konnte an beiden Stationen aus Sicherheitsgründen nicht durchgeführt werden (starker Schwell und Unfallgefahr durch die Bauart der malaysischen Boote). FS Sonne wurde dreimal vom Forschungsflugzeug Falcon, das während der Kampagne in Miri (Borneo) stationiert war, zur Interkalibrierung und zur Verfolgung identischer Luftmassen tief überflogen (siehe Abbildung 1). Im Mai 2012 fand ein Auswertungstreffen am GEOMAR in Kiel statt, auf dem gemeinsame Publikationen geplant und besprochen wurden.

## I.4. STAND DER WISSENSCHAFT UND TECHNIK

Die im Frühjahr über den Polen auftretende chemische Ozonabnahme wird hauptsächlich durch anthropogen emittierte Chlor- und Bromfluorkohlenwasserstoff verursacht. In den mittleren Breiten bestimmt ebenfalls die Zufuhr von Halogenen den stratosphärischen Ozonhaushalt und die starke Ozonabnahme. Neuen Erkenntnissen zur Folge spielen hier auch natürliche Halogenkohlenwasserstoffe eine Rolle (Salawitch et al., 2005, 2006; WMO, 2007). Neue Ergebnisse zeigen, dass in der unteren Stratosphäre höhere Konzentrationen reaktiven Broms auftreten, als durch die Emissionen der langlebigen, meist anthropogenen Spurengase erklärt werden können (Dorf et al., 2005, Dorf et al., 2006, WMO 2011). Unter Berücksichtigung von 5 ppt zusätzlichem reaktiven Brom kann in Chemietransportmodellen (CTM) die beobachtete Ozonabnahme in mittleren Breiten simuliert werden (Salawitch et al., 2005; WMO, 2011; Sinnhuber et al., 2009). Als Hauptverdächtige für dieses Brom gelten ozeanische Emissionen kurzlebiger Bromverbindungen, insbesondere von Bromoform ( $\text{CHBr}_3$ ) und Dibrommethan ( $\text{CH}_2\text{Br}_2$ ) (Quack und Wallace, 2003) (Abbildung 2), die laut Modellstudien einen großen Anteil an den +5 pptv Totalbromgehalt in der Stratosphäre haben (Hossaini et al., 2010; Gettelman et al., 2009; Aschmann et al., 2009; Tegtmeier et al., 2012) oder sogar komplett die zusätzlichen 5 pptv Brom in der Stratosphäre verursachen (Liang et al., 2009) können.

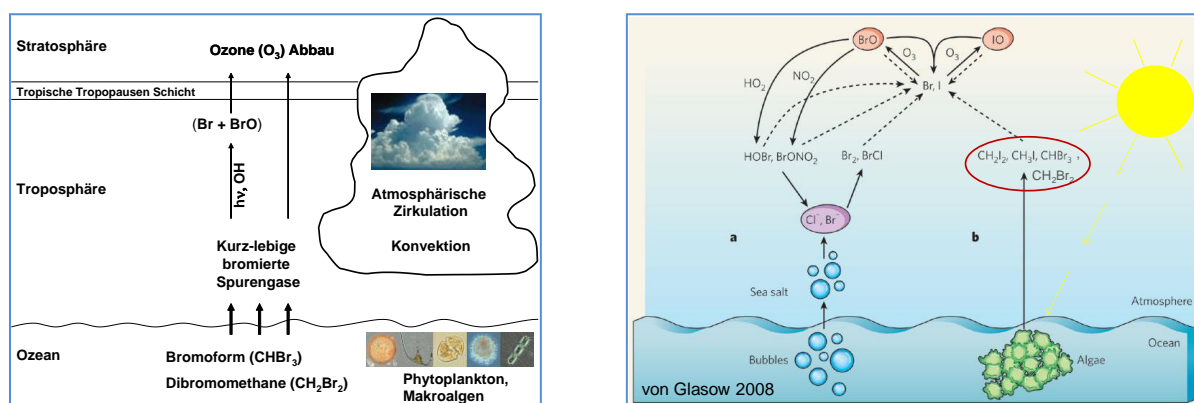


Abbildung 2: Ozeanische Quellen kurzlebiger Halogenkohlenwasserstoffe und ihre Wirkungen in der Atmosphäre. Rechte Abbildung von Glasow (2008).

Ein großer Anteil der ozeanischen Emissionen befinden sich in tropischen Regionen, wobei stark lokalisierte Quellregionen in Küstennähe, im äquatorialen Atlantik und im nordwestafrikanischen Auftriebsgebiet vor Mauretanien identifiziert wurden (Quack et al., 2004; Quack et al., 2007a; Butler et al., 2007). Die ozeanischen Quellen sind weitgehend unerforscht, werden jedoch im Allgemeinen mit biologischer Produktion in Verbindung gebracht. Eine wichtige Produzentenrolle von bromierten Verbindungen spielen küstennahe Makroalgen (Carpenter und Liss, 2000), jedoch ist auch die biologische Produktion der Hauptverbindung Bromoform ( $\text{CHBr}_3$ ) in der Oberfläche des offenen Ozeans, wie es im tropischen und subtropischen Atlantik gefunden wurde (Quack et al., 2004, 2007a, b) nicht zu vernachlässigen. Die genaue Beziehung der Halogenkohlenwasserstoffproduktion zur Phytoplanktonverteilung ist bis heute unklar. Als Faktoren, die die ozeanischen Konzentrationen beeinflussen, kommen unter anderem der Küstenabstand und die Wassertiefe, die Spezieszusammensetzung und Lebenszyklen des Phytoplankton, Wassertemperatur sowie Vermischung und Gasaustausch in Frage (Carpenter et al., 2012).

Auch jodierte Kohlenwasserstoffe, wie Jodmethan ( $\text{CH}_3\text{I}$ ) können eine Bedeutung für die Ozonchemie (Solomon et al., 1994, Vogt et al., 1999, Tegtmeier et al., 2013) und für weitere chemische Prozesse in der Atmosphäre haben (Kolb, 2002, O'Dowd et al., 2002). Die Hauptquelle für atmosphärisches



Jodmethan ist die Emission aus dem Ozean, wobei die Produktionswege im Ozean nur zu 10% aufgeklärt wurden und photochemische sowie biologische Ursachen haben können (Richter und Wallace, 2004). Simultane Messungen der halogenierten Spurengase in der Atmosphäre und im Ozean sind rar (WMO, 2011) und bisher nur in wenigen Veröffentlichungen zu finden, an denen wir maßgeblich beteiligt sind. Die simultanen Messungen sind notwendig, um die ozeanischen Emissionen berechnen zu können, von denen große Mengen durch Konvektionsprozesse in die obere Atmosphäre transportiert werden können. Eine Messkampagne, die sowohl die ozeanischen Emissionen mittels der Untersuchungen auf einem Forschungsschiff, als auch ihre Transportwege durch die Atmosphäre mit Flugzeugmessungen bis in die obere Troposphäre untersucht, war bisher noch nicht durchgeführt worden.

Die tropische Tropopausenschicht (Tropical Tropopause Layer: TTL) in ca. 14 -18 km Höhe ist das Eintrittstor für troposphärische Spurengase in die Stratosphäre (Abbildung 3).

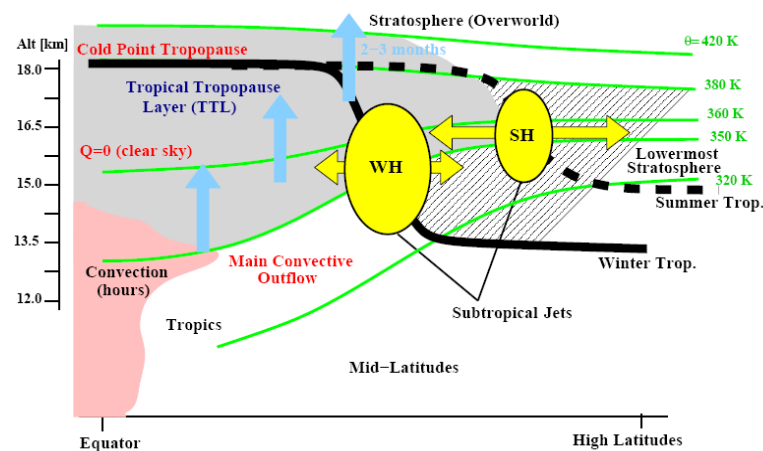


Abbildung 3: Die atmosphärische Zirkulation von Spurengasen. Schema von Transportprozessen, die die Tropische Tropopause mit der Stratosphäre verbinden (Konopka et al., 2007).

Die dynamischen und mikrophysikalischen Prozesse in der TTL, die die konvektionsgetriebene Troposphäre, mit zum Teil sehr schnellen Aufstiegsgeschwindigkeiten (einige m/s) von der darüber liegenden Stratosphäre (15-50 km Höhe) mit langsamen, strahlungsgetriebenen Vertikalbewegungen (mm/s) trennt, sind von großer Bedeutung für den Spurengaseintrag und die chemische Zusammensetzung der Stratosphäre. Mit neuen Methoden konnten realistischere Verweildauern in der TTL berechnet werden (Krüger et al., 2009), die zu einer besseren Abschätzung der absoluten Transportwege der sehr kurzlebigen Gase führen konnten (WMO, 2011). Dadurch ergibt sich eine genauere Aussage über die Eintragsorte von Luftmassen in die Stratosphäre (Krüger et al., 2008) und über die Form der Spurengase, die die Stratosphäre entweder als sog. Quell- oder Primärgase (mit Lebenszeiten von einigen Wochen) oder sog. Sekundärgase erreichen, die durch homogene und heterogene atmosphärenchemische und mikrophysikalische Prozesse innerhalb von Wolken aus den Quellgasen entstehen (WMO, 2007). Der tropische Pazifik wurde als Sektor für den Haupteintragsort von Luftmassen innerhalb der TTL im NH- Winter identifiziert (Fueglistaler et al, 2004; Bonazzola und Haynes 2004; Krüger et al., 2008). In diesem Gebiet sind auch die schnellen Aufstiegszonen der vorherrschenden tropischen Konvektionstürme lokalisiert (Abbildung 4).



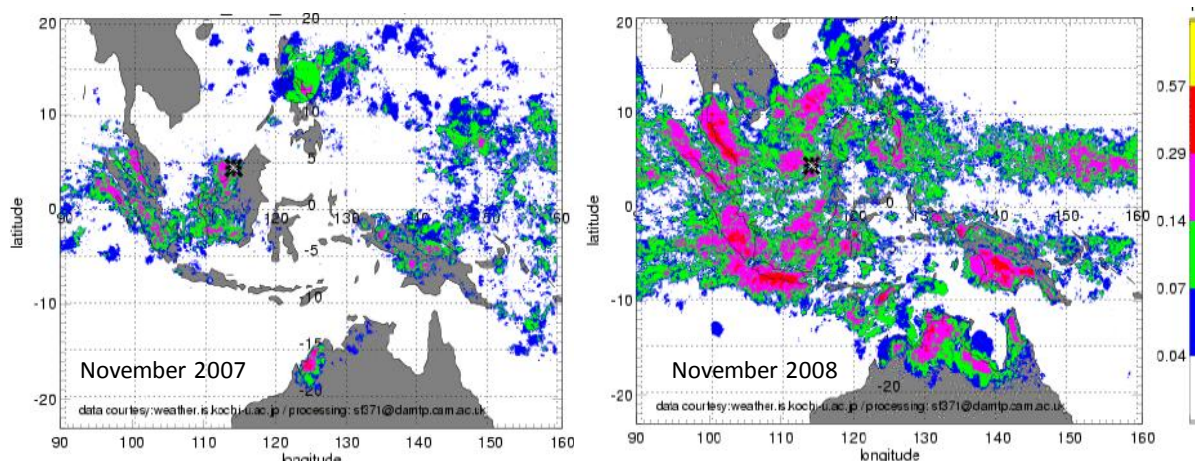


Abbildung 4: Beispiel des vertikalen Luftmassentransports in die tropische Tropopausenschicht im November der Jahre 2007 und 2008. Dargestellt ist die Konvektionswahrscheinlichkeit  $p$ . (Fueglistaler personal communication).

Marine Emissionen in der Nähe des Maritimen Kontinent (Bezeichnung des inselreichen Gebietes des tropischen Südwest Pazifik, 90°E - 150° E) waren unbekannt, da es aus diesem Gebiet bisher keine ozeanischen Messungen gab (Abbildung 5). Es konnte vermutet werden, dass die Gewässer um den west-pazifischen maritimen Kontinent eine bedeutende Quellregion mariner, halogenierter Verbindungen für die Atmosphäre darstellt. Makroalgenreiche Küsten und Organismen in Korallenriffen, von denen viele durch ihren Enzymgehalt an Haloperoxidasen (Gribble, 2000) als mögliche Halogenkohlenwasserstoffproduzenten in Frage kommen und hohen Wassertemperaturen können zu starken Emissionen beitragen.

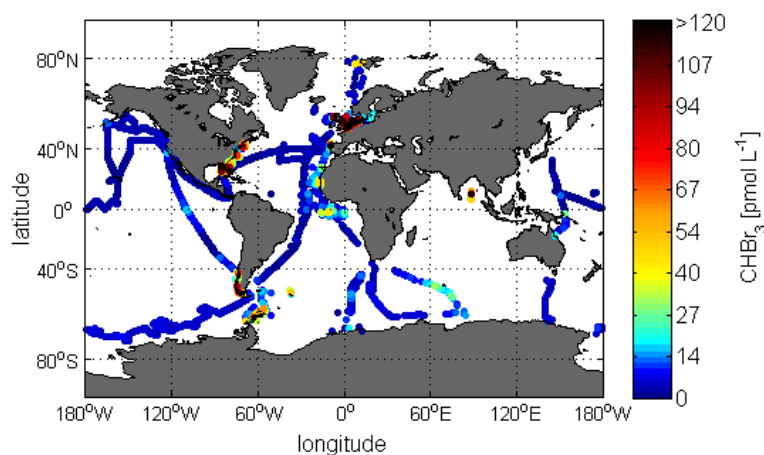


Abbildung 5: Messungen von Bromoform im Meerwasser (Daten aus <http://halocat.geomar.de>, initiiert in Mai 2009).

Resultierend aus den allerersten Messungen dieser Verbindungen im Westpazifik (140°-150°E) auf einem Transit mit FS Sonne über 60 Breitengrade (TransBrom) im Jahr 2009 (Quack und Krüger, 2010, Krüger und Quack, 2013) wurde bestätigt, dass der tropische Westpazifik ein Haupteintragsgebiet für kurzlebige marine Bromverbindungen in die Stratosphäre darstellt (Tegtmeier et al., 2012). Aus dem globalen Hauptkonvektionsgebiet im tropischen Westpazifik existierten bisher nur die ozeanischen Messungen der ersten Sonne Expedition TransBrom-Sonne (Oktober, 2009, Abbildung 5), die während niedriger Aktivität der atmosphärischen Konvektion im Oktober 2009, in

einem weitgehend biologisch ärmeren und küstenfernen Seegebiet des Westpazifik stattfand (Quack und Krüger, 2010, Krüger und Quack, 2013). Nun sollte die SHIVA-SONNE Kampagne in der Hauptkonvektionszeit in biologisch reicheren und küstennäheren Gewässern durchgeführt werden, die zudem auch zu Beginn der Hauptkonvektionszeit lag.

Mit Hilfe der Schiffskampagne und anschließender Auswertung und Modellierung der Ergebnisse sollte in Zusammenarbeit mit atmosphärischen Dynamikern und Chemikern geklärt werden, wie stark der Beitrag der dortigen Emissionen am Halogengehalt in der Stratosphäre ist. Weiterhin sollten die biologischen Quellen auch für die halogenierten und andere reaktive Spurengase in der Atmosphäre bestimmt werden. Aus dem Bereich des „maritimen Kontinent“ lagen bisher keine ozeanischen Messungen klimarelevanter Spurengase vor. Die internationale Messkampagne unter Kombination eines großen und mehrerer kleiner Forschungsschiffe, eines Forschungsflugzeuges, sowie gleichzeitige Messungen vom Erdboden und vom All aus, wie sie im tropischen Westpazifik für den Frühwinter 2011 zur Untersuchung der ozeanischen Emissionen an halogenierten Kohlenwasserstoffen, ihren atmosphärischen Transportwegen sowie die Auswirkung dieser Verbindungen für die globale Ozonschicht im Rahmen des EU- SHIVA Projektes geplant und erfolgreich durchgeführt wurde, ist bisher weltweit einmalig.

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## I.5. ZUSAMMENARBEIT

Die Ausfahrt SO218 (SHIVA-Sonne), auf der ein großer Teil der Zusammenarbeitskosten mit den malaysischen Wissenschaftlern vom BMBF unterstützt wurde, war Bestandteil des EU-Projektes SHIVA (Stratospheric halogens in a varying atmosphere, EU FP7 Grant: 226224).

Teilnehmer der SO218 Fahrt und auch des Projektes SHIVA sind an weiteren nationalen und internationalen Projekten beteiligt, von denen einige im Folgenden aufgelistet sind:

- EU: SCOUT-O3 (Stratospheric-Climate Links with Emphasis on the Upper Troposphere and Lower Stratosphere-O3)
- EU: COST-Action 735 (Tools for Assessing Global Air-sea fluxes of Climate Gases)
- SPARC (Stratospheric Processes And their Role in Climate)
- CCMVal (coupled Chemistry-Climate Model Validation/ Stratospheric Processes and their Role in Climate (CCMVal/ SPARC)-Initiative)
- IGBP (International Geosphere-Biosphere Programme)/ IGAC (International Global Atmospheric Chemistry) / SOLAS (Surface Ocean Lower Atmosphere Study)
- BMBF-Verbundprojekt: SOPRAN (Surface Ocean Processes in the Anthropocene)
- IGAC/SOLAS/ HIT (Halogens in the Troposphere)
- WGL-Projekt: TransBrom,
- BMBF-Programm ROMIC: Role of the middle atmosphere in climate,
- Projekt: THREAT- The role of oceanic halogen and sulfur compounds for the middle atmosphere

An der Forschungsreise nahmen neben den an Bord befindlichen Wissenschaftlern, unter anderem folgende Institutionen und Partner mit der aufgeführten Beteiligung als hauptverantwortliche Wissenschaftler teil:

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Weitere Projekte und Partner befinden sich auf der SHIVA-homepage: <http://shiva.iup.uni-heidelberg.de/links.html>

Die SO218-Forschungsfahrt war ein wesentlicher Bestandteil des EU-Projektes SHIVA, dass im Rahmen des 7. Forschungs Rahmenprogramm der EU (SHIVA- Halogen Impacts in a Varying Atmosphere) die koordinierte Probennahme im tropischen West-Pazifik auf einem Forschungsschiff mit dem gleichzeitigen Einsatz eines Forschungsflugzeuges vorsah. Es fand eine enge Kooperation mit Wissenschaftlern des GEOMAR im Rahmen des BMBF-Verbundprojektes SOPRAN statt, die sich mit den ozeanischen Emissionen klimarelevanter Spurengase beschäftigen, da es aus diesem Ozeangebiet bisher kaum Messdaten gibt. Aufgrund der Einmaligkeit des Forschungsvorhabens bestand großes Interesse von Wissenschaftsgruppen sich an der Schiffskampagne im tropischen Westpazifik zu beteiligen, die zu einem über das Kernthema hinausreichenden Erfolg der Forschungsseereise beigetragen haben.

## II. 1. VERWENDUNG DER ZUWENDUNG UND ERGEBNIS

Die SO218 Fahrt des Forschungsschiffes SONNE führte vom Starthafen Singapur, Abfahrt am 15.11.2011, bis nach Manila, Philippinen, Ankunft am 29.11.2011 (Abbildung 1). Alle Luftfrachten, Chemikalien und der bestellte flüssige Stickstoff wurden bis kurz vor Abfahrt in Singapur pünktlich geliefert. Somit konnte die Zeit im Hafen gut genutzt werden, um fast alle Instrumente dort aufzubauen. Der unermüdliche Einsatz der 25 Wissenschaftler an Bord, die von der Besatzung tatkräftig unterstützt wurden, ermöglichte es, dass bereits beim Auslaufen die meisten der 70 Mess-, Analyse- und Probenahmesysteme liefen, die einen einmaligen Datensatz produzierten, da in diesen Gewässern die meisten der auf SO218 untersuchten Parameter (unterschiedlichste Spurengase und physikalische Eigenschaften in Atmosphäre und Ozean, sowie biologische Eigenschaften des Wassers) noch nie untersucht worden waren. Die Instrumente konnten schon beim Einlaufen in malaysische Hoheitsgewässer vier Stunden nach Abfahrt in Singapur erste Daten aufzeichnen. Nach sechzehn Stunden Fahrtzeit führte die SO218 Route über einen Nordschlenker durch Indonesisches Gewässer, in denen keine Wasserproben gewonnen wurden, zur malaysischen Westküste von Borneo (Abbildung 1). Nach einer Tagestation trafen wir, wie verabredet am Samstag, den 19. November in der Mittagszeit ein lokales Fischerboot, besetzt mit vierzehn malaysischen, deutschen und englischen Wissenschaftlern und einem Fernsichteam (Abbildung 6). Seegangsbedingt konnte das kleine Fischerboot leider nicht längsseits gehen, so dass die Gäste nicht an Bord kommen konnten. Die Proben von fünf küstennahen Stationen konnten jedoch erfolgreich ausgetauscht werden und wurden

an Bord dann direkt auf biologische und chemische Parameter untersucht, um den Gradienten der Spurengaskonzentrationen zwischen offener See und Schelfgebiet zu bestimmen.



Abbildung 6: Küstenboot mit malaysischen Kollegen aus Kuching mit küstennah gewonnenen Proben ( 19. November 2011).

Gleichzeitig überflog das Forschungsflugzeug der DLR (Deutsche Luft- und Raumfahrt) Falcon dessen Standort extra für diese Kampagne nach Miri auf Borneo gelegt wurde, die Sonne (Abbildung 7) und beprobte die Atmosphäre im Tiefflug neben der Sonne, etwa in gleicher Höhe, in der an Bord auch Spurengase aus der marinen Grenzschicht beprobt wurden.



Abbildung 7: Grenzschichtmessungen von Falcon und Überflug vor Kuching (Fotos von Torsten Bierstedt und Johannes Lampel).

Auch in Kota Kinabalu konnten küstennahe Proben am 22. November 2011 an Bord genommen werden, wobei auch dieses Mal der Seegang und die Bauart des Bootes ein sicheres Anlegen an der SONNE verhinderte. Beim zweiten Besuch der Falcon am 22. November 2011 wurde im Tiefflug wieder nahtlos an unsere Probenahme angeschlossen, während beim dritten Besuch im Nordosten Borneos Profile in der oberen Troposphäre, ohne Sichtkontakt mit Sonne geflogen wurden (Abbildung 7).

Während der vierzehntägigen dauernden Reise wurden rund um die Uhr in ein bis dreistündigem Rhythmus Wasser-, Luft-, Phyto- und Zooplanktonproben untersucht, sowie mehrere chemische und physikalischen Parameter von Atmosphäre und Meerwasser kontinuierlich aufgezeichnet. Auf 14 Stationen wurden 26 CTD Profile gefahren und 40 Außenbordseinsätze von Lichtmessinstrumenten und Planktonnetzen durchgeführt. Mehr als 3000 Wasserproben wurden gewonnen, in denen mehr als 40 verschiedene chemische und biologische Parameter- entweder direkt an Bord oder später in den



Heimatlaboren analysiert wurden. Mit 73 Radio- und 6 Ozonsonden, 400 Kanister- und Direktluftproben, sowie 9 kontinuierlich messenden optischen Systemen und Massenspektrometern wurde der Spurengasgehalt der Luft untersucht.

Die gewonnenen Daten führten schon zu interessanten Ergebnissen (Part 2: Reports 1-14 (24 Einzelberichte)) gemeinsamen Auswertungen, Präsentationen und Publikationen (Part 2: Tabelle 4) und bilden auch weiterhin eine gute Grundlage für zukünftige Arbeiten (II.3). Im Folgenden wird eine Übersicht in deutscher Sprache über die Ergebnisse der beteiligten Arbeitsgruppen gegeben, deren ausführliche Berichte in englischer Sprache im 2. Teil des Berichtes zu finden sind. Diese Art der Präsentation wurde gewählt, um dem internationalen Charakter der Expedition Rechnung zu tragen und einen Abschlussbericht für alle an der Seereise beteiligten Gruppen zu erhalten, die weitere gemeinsame Auswertungen und Kooperationen erzielen soll. Am 15. September 2013 wurde auch der endgültige Abschlussbericht für das EU-Projekt SHIVA in Brüssel eingereicht, in den Ergebnisse dieser Arbeiten einfließen. In den Zeitschriften *Atmospheric Chemistry and Physics* und *Biogeosciences* wurde der Spezialband: *The EU Project SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere)* für Veröffentlichungen aus der SHIVA-Kampagne eingerichtet.

Die regelmäßigen Luftanalysen und Radiosondenaufstiege an Bord der Sonne (**Part 2 Report 5**) die eine eher spurengasarme Luft mit Kontaminationsereignissen zeigten (**Part 2 Report 6, 8, 9,10a**), wurden durch eine intensive Bebrobung ozeanischer Parameter ergänzt. Die Analyse der marinen Spurengase in der Wassersäule zeigte erhöhte Konzentrationen der jodierten und bromierten Verbindungen (**Part 2 Report 1**). Diese Übersättigung des Meerwassers führte bei einer variablen Windgeschwindigkeit meist zu einem erhöhten Fluss der Verbindungen aus dem Meerwasser (**Part 2 Report 1**). Aufgrund der starken konvektiven Aktivität wurden schnelle und starke vertikale Transporte der Luftmassen in der marinen Grenzschicht bis in die Stratosphäre modelliert (**Part 2 Report 14**) und gemessen (**Part 2 Report 10b**), die bestätigten, dass die Region Quellen mariner halogenierter Spurengase für die Stratosphäre besitzt. Die Tiefenprofile des Meerwassers an den Stationen zeigten große Unterschiede in der Ozeanschichtung, als auch in der Tiefe des Chlorophyllmaximums. Dadurch konnten Aussagen über die Herkunft der marinen halogenierten Spurengase getroffen werden (**Part 2 Report 1**).

Mittels zweier unabhängiger Messsysteme (Purge- und Trap Gaschromatographie) wurden die marinen und die atmosphärischen Konzentrationen von Jodomethan, Dichlormethan, Chloroform, 1,1,1 – Trichlorethan, Tetrachlorkohlenstoff, 1,1,2 – Trichloroethen, Dibrommethan, Dichlorobrommethan, Chlorjodmethan, 1,1,2 – Trichlorethan, Dibromchlormethan, Bromjodomethan, Bromoform, Dijodmethan an Bord der Sonne analysiert. Die Ergebnisse zu den **Halogenierten Kohlenwasserstoffen in Meerwasser und Atmosphäre** (Birgit Quack, Eliot Atlas, Stefan Raimund, Helmke Hepach, Qiang Shi, Gert Petrick) zeigen unter anderem generell hohe Konzentrationen brom- und jodhaltiger Verbindungen im Wasser, die in den flachen Schelfregionen und nah den Küsten stellenweise stark erhöht waren und ihre Quellen in Küstennähe und unterhalb der ozeanischen Deckschicht besaßen (**Part 2 Report 1**). Auch die niedrigen Gehalte der Spurenstoffe in der Atmosphäre führten zu einer Übersättigung des warmen Meerwassers, das überall eine Quelle der natürlichen Halogenverbindungen für die Atmosphäre darstellte, die im Verlauf weniger Stunden in die mittlere und obere Troposphäre transportiert werden können (**Part 2 Report 5, 14**).

Das Ziel der **Beobachtung der globalen Phytoplanktonverteilung und Produktivität mit Hilfe von in situ Messungen und Satellitenfernerkundung (Ozeanoptik)** (Astrid Bracher, Rizman Idris, Aazani Mujahid, Joseph Palermo) war es durch die kombinierte Nutzung von Techniken der Satellitenfernerkundung und in-situ Messungen der Ozeanoptik, der Phytoplanktonproduktivität und Zusammensetzung, Abschätzungen der globalen Primärproduktion und Verteilung wesentlicher



Phytoplankton-Gruppen, besonders in Küstenregionen zu verbessern (**Part 2 Report 2a**) Die Messungen werden als Referenzspektren für Satellitendatenauswertungen, Strahlungstransportrechnungen und ebenso für die Validation der Algorithmen genutzt.

Die Messungen des AWI wurden dabei durch Messungen der malaysischen Universitäten UM in Kuala-Lumpur (Dr. Rizman Idid: Phytoplanktonbiomassemessungen und Primärproduktionsbestimmung durch fluorometrische Methoden: PAM, Turnerfluorimeter, Phytoplankton und Zooplanktondiversitätsbestimmungen durch Mikroskopie und Zählung der Netzfänge) UNIMAS Kuching (Dr. Aazani Mujahid: morphologische und molekularbiologische Charakterisierung der Phytoplankton und Bakteriendiversität, DNA-Proben, CTD, Chl-a: Satellit/in-situ Vergleiche) , UMS Kota-Kinabalu (Prof. Dr. Ann Anton: Biogeographische Herkunft und phylogenetische Beziehungen of *Cochlodinium polikrikoides*) University of the Philippines Diliman, Quezon (Dr. Joseph Palermo: Phytoplanktonspezies und Zusammensetzung mit FlowCam und Infinity ME) ergänzt (**Part 2 Report 2b, 2c, 2d, 13 a, 13b, 13c**). Die biologischen Analysen vertieften das Verständnis über die Quellen und Senken der halogenierten und anderen Spurengase im Ozean.

Der Zusammenhang zwischen den Gemeinschaften des Zooplanktons und des Phytoplanktons sollten im Hinblick auf die Hauptspezies und taxonomischen Gruppen charakterisiert werden. Zum Sammeln und Filtern der Zooplanktonproben wurden Planktonnetze benutzt. Die Proben sollten zur morphologischen Identifikation in mit Formalin gepufferten Seewasser und zur molekular/genetischen Untersuchungen in Alkohol aufbewahrt werden. Aus Sicherheits- und Lufttransport Gründen wurde auf den Kauf von Formalin verzichtet und auf Wunsch des malaysischen Kollegen unvergällter Alkohol in Singapur bei der Firma Merck beschafft. Bisher wurden die Proben leider nicht von den Projektpartnern ausgewertet.

Ozeanische und besonders küstennahe Emissionen der **Klimarelevanten Spurengase: DMS, N<sub>2</sub>O und CH<sub>4</sub> in Ozean und in der Atmosphäre (Christa Marandino, Cathleen Zindler, Hermann Bange)** die direkt und indirekt das Erdklima und die Chemie der Erdatmosphäre entscheidend beeinflussen, sind eine starke Quelle für die Troposphäre. Es wurden Messungen dieser Gase in den Küstenregionen und flachen Schelfgebieten des Südchinesischen Meers und der Sulusee durchgeführt, um die Quellstärke dieser Region und damit ihre Rolle für den atmosphärischen Haushalt von DMS, N<sub>2</sub>O und CH<sub>4</sub> abschätzen zu können. Es wurden starke Quellen dieser Gase besonders an der Küste Borneos (**Part 2 Report 3**) gefunden.

**Kohlendioxid und Sauerstoff (Tobias Steinhoff, Arne Körtzinger)** wurden im Gebiet des Südchinesischen Meeres gemessen und sollen zur Identifikation und Quantifikation von CO<sub>2</sub>- und O<sub>2</sub>-Quellen und -Senken, und zur Separation physikalischer und biologischer Faktoren für beobachtete Quellen/Senken beitragen. Die Messungen ergänzen die wenigen vorhandenen Daten dieser Gase im Bereich des tropischen West-Pazifik in Küstennähe und auf Schelfen. Aufgrund der Dynamik der biogeochemischen Prozesse auf den Kontinentalschelfen, der tropischen Lage und den terrestrischen Einflüssen war die Region durch Disäquilibriums in CO<sub>2</sub> und O<sub>2</sub> gekennzeichnet, was bisher nicht untersucht und dokumentiert wurde. Generell ist die Region entlang der SO218- Fahrtroute eine CO<sub>2</sub>-Quelle für die Atmosphäre, während der Oberflächenozean häufiger leichte Sauerstoffuntersättigungen aufweist (**Part 2 Report 4**).

Es wurden intensive **Radiosondierungen (Kirstin Krüger)** und sechs Ozonsondierungen während der Seereise von Singapur nach Manila (Philippinen) durchgeführt. Die so gewonnenen meteorologischen Daten ergaben Aufschluss über den vertikalen Aufbau der Atmosphäre und wurden für die Modellierung des Transports von Spurengasen vor allem in der freien Troposphäre und der tropischen Tropopausenschicht verwendet. Weiterhin lieferten diese Messungen notwendige Beiträge

zu Strahlungstransportrechnungen und für die Bestimmung der Mischungsschichthöhe. Damit wurden Spurengasprofile von den Messinstrumenten (z.B. MAX-DOAS) während der Kampagne erstellt und der Transport von Spurengasen aus der marinen atmosphärischen Grenzschicht bis in die Stratosphäre berechnet (**Part 2 Report 5**)

Ein- bis dreistündig gewonnene Kanisterluftproben zur **Bestimmung der Spurengaskonzentration in der marinen Grenzschicht (Elliot Atlas)** wurden in Miami analysiert. Die Probenahmehäufigkeit wurde an den beiden Tagesstationen und an der Nordostküste Borneos erhöht. In den Kanistern werden 70 verschiedene, meist anthropogene aber auch natürliche atmosphärische Spurengase (z.B.: Fluorchlorkohlenwasserstoffe, Alkane, Alkylnitrate, Brom-, Chlor- und Jodverbindungen) analysiert, um ihre Quellen, den Transport und die Umwandlungen in der globalen Atmosphäre zu charakterisieren. Die Spurengasgehalte in der Atmosphäre waren niedrig, wobei erwartungsgemäß in Landnähe und in der Nähe von Bohrinseln lokale Kontaminationsquellen für Kohlenwasserstoffe gefunden wurden. Die halogenierten Spurengase waren generell vorhanden und nicht so variabel wie die anthropogenen Verbindungen (**Part 2 Report 6**).

Mittels spektroskopischer Multi-Axis-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy) Messung wurde die Konzentration **anorganischer Spurengase (Ulrich Platt, Klaus Pfeilsticker, Folkard Wittrock)**, darunter freie Halogenradikale (BrO, IO), innerhalb der tropischen marinen Grenzschicht bestimmt, sowie Aussagen über deren Höhenverteilung getroffen. BrO und IO, die eine wichtige Rolle in der Photochemie von Ozon spielen und die troposphärische Oxidationskapazität beeinflussen wurden gemessen. Das zum Vergleich mitgeführte neuartige „Cavity- Ring Down“ Spektrometer zur Messung von IO zeigte Werte zwischen 0.5 and 2 ppt und leicht höhere Werte in der Sulu See, während BrO generell unterhalb der Detektionsgrenze lag (**Part 2 Report 7**).

Zur Analyse der Herkunft und zur Charakterisierung der chemischen Zusammensetzung der Luftmassen, fanden in situ Messungen ausgewählter **atmosphärischer Spurengase CO, CH<sub>4</sub>, CO, O<sub>3</sub> (Hans Schlager, Tina Jurkat, Dominik Schäuble, Christiane Voigt, DLR)** statt. Diese Messungen zeigten eine leicht verschmutzte atmosphärische Mischungsschicht mit erhöhten Quellen in der Nähe der größeren Städte, in deren Nähe auch Halogenfreisetzung durch Säureaustauschreaktionen beobachtet werden konnten (**Part 2 Report 10a**). Mit Hilfe von Tracermessungen wurde die Zusammensetzung der Grenzschicht im Südchinesischen Meer charakterisiert und diese Daten zusammen mit entsprechenden Messungen an Bord des Forschungsflugzeuges Falcon im Ausströmgebiet von Konvektionszellen analysiert (**Part 2 Report 10b**).

Messungen von anorganischen Iodspezies **IO, I<sub>2</sub> und HOI+ICl (Hannah Walker, Dwayne Heard)** zeigten Maxima der reaktiven Iodspezies IO im Nordosten von Borneo, die nicht mit einer physikalischen Messgröße oder Chlorophyll korrelierten, jedoch negativ mit molekularem Iod I<sub>2</sub> und ozeanischem Methyljodid und Chlorigomethan korreliert waren. Die atmosphärischen Gehalte von HOI und ICl wurden erstmalig über dem Ozean gemessen (**Part 2 Report 10a und 10b**)

Während der Fahrt wurden tägliche Proben atmosphärischer **Aerosole (Alex Baker)** gewonnen, die auf Trockeneis nach Norwich transportiert und dort auf ihre Hauptbestandteile sowie Chlor-, Brom- und Iodspezifikationen analysiert wurden. Es bestätigte sich, dass die Aerosole in der marinen Atmosphäre beim Halogenkreislauf eine Schlüsselrolle spielen, indem Brom durch die Reaktion mit Ozon an Meersalzpartikeln in die Gasphase überführt wurde. Die Aerosole waren abgereichert, bromärmer als das Meerwasser und damit eine Bromquelle für die Gasphase). Aerosole scheinen damit eine Quelle für reaktives Chlor und Brom und eine Senke für Jod zu sein, dass sich in den Aerosolen stark anreicherte (**Part 2 Report 11**).

In der Sulu See wurden an vier tiefen Stationen anthropogenen Fluorchlorkohlenwasserstoffe als **transiente Tracer (Toste Tanhua)** analysiert, um das Alter der Wassermassen und den Gehalt von anthropogenem Kohlenstoff in der Sulusee zu analysieren. Die Ergebnisse zeigen, dass das Bodenwasser in der Sulusee sehr alt (400 bis 600 Jahre) ist und dass die Sulusee nur geringe Mengen anthropogenen Kohlenstoffs enthält (**Part 2 Report 12**).

Es wurde in Kooperation mit mehreren malaysischen Universitäten drei **lokale Küstenbootseinsätze** durchgeführt auf denen unter anderem **Untersuchungen zur schädlichen Algenblüten (SAB) und Vergleich der Wasserqualität der Westküste Sabahs und anderer Küstengewässer Borneos** (**Moritz Müller, Aazani Mujahid, Felicity Kuek, Hong-Chang Lim, Sing-Tung Teng, Chui-Pin Leaw, Lim Po Teen, Ann Anton**) stattfanden. Als Teil der komplementären dreiteiligen Reihe von lokalen Ausfahrten in Kuching, in Kota Kinabalu und in Semporna wurden zwei Transekte in Kuching am 16. und 19. November 2011 unternommen, wobei der Transekt am 19. November mit einem Probenaustausch mit der Sonne kombiniert wurde. Luft- und Wasserproben wurden an 5 Stationen mit Abständen von 5 km, bis zu 20 km vor der Küste gesammelt (siehe Abbildung 1).

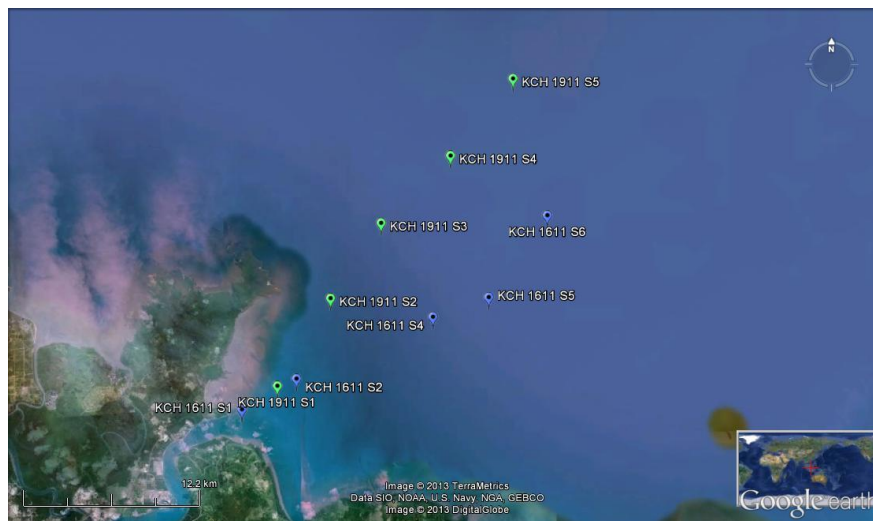


Abbildung 1: Übersicht der Messstationen in Kuching, Sarawak .

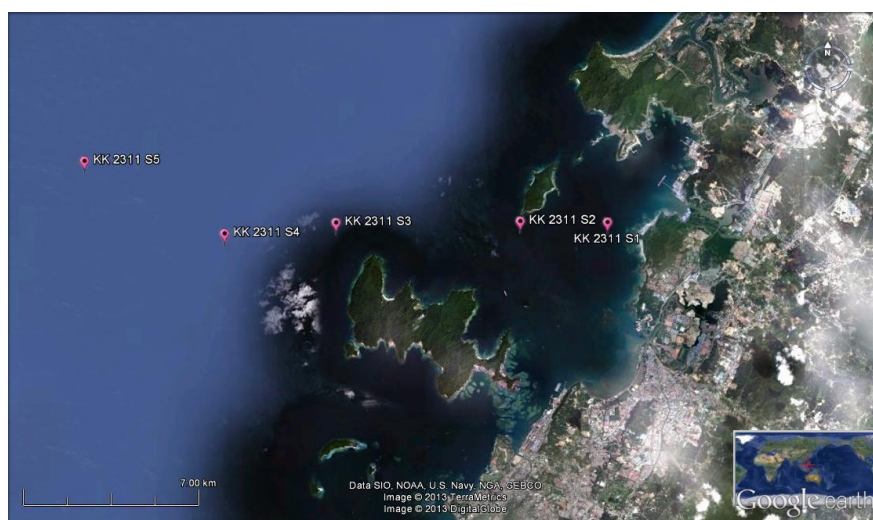


Abbildung 3: Übersicht der Messstationen in Kota Kinabalu, Sabah.

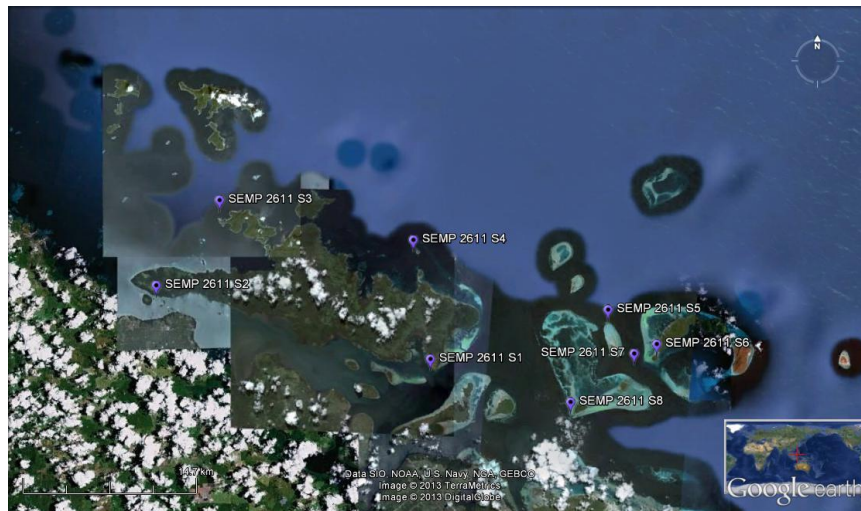


Abbildung 4: Übersicht der Messstationen in Semporna, Sabah.

Die Hauptziele der lokalen Ausfahrten waren: (i) küstennahe Proben zur Ergänzung der offenen Ozean Proben von der FS Sonne, der Falcon Flugzeug Daten und der Satelliten Daten zu erhalten (ii) Proben, die an der Küste gesammelt waren, auf die Sonne für weitere Analysen (z.B. VLS und Nährstoffe) weiterzugeben und Proben von der FS Sonne (sensible biologische Proben) an das Küstenboot für weitere Analysen in den UNIMAS und Swinburne Laboren zu überreichen. Zu den gemessenen Parametern gehörten halogenierte Spurengase in Meerwasser und Luft (GEOMAR, UEA, UM), Plankton (UNIMAS, UMS) und ausgewählte Oberflächen Wasser-Parameter (UNIMAS, SUTS). Des Weiteren wurden Proben gesammelt, um Informationen über die bakteriellen Gemeinschaften in Kuching zu erhalten. All diese Daten können mit den Daten aus den anderen lokalen Booten (Kota Kinabalu und Semporna) verglichen werden, wie zum Beispiel die Zusammensetzung der bakteriellen Gemeinschaften im Hinblick auf *in-situ* physikalisch-chemische Wasserparameter. Die erste Station in Kuching zeigte einen sichtbaren Einfluss von Flusswasser wie zum Beispiel einen geringen Salzgehalt von 28 und einen pH-Wert von 7,90 an der Oberfläche. Der Einfluss des Sarawak-Flusses war auch an deutlich höheren Nitrat, Phosphat, Nitrit, und Silikat Werten sichtbar (**Part 2 Report 12**). Nährstoffgehalte in Kuching waren in der Regel höher als in Kota Kinabalu. Um Unterschiede in der Verteilung in der oberen Deckschicht zu beurteilen, wurden auch Proben in 5 m Tiefe genommen. Aus Kuchings' Gewässern wurden 89 bakterielle Isolate während der beiden Ausfahrten (16. November und 19. November 2011) gewonnen. Die bakterielle Gemeinschaft hatte Vertreter der Alpha-, Beta- und Gamma - proteobacteria sowie der Firmicutes; die Vielfalt war jedoch eng mit der Tiefe der Proben verbunden (**Part 2 Report 2c**). Bakterien aus Kuching zeigten die höchste Fülle von den beiden untersuchten DMSP-degradierenden Genen (36%) im Vergleich zu bakteriellen Gemeinden von Kota Kinabalu und Semporna (13% und 19%). Die Ergebnisse zeigen, dass die Gemeinschaftsstruktur der Gammaproteobacteria in Kuching's Gewässern eng mit dem lokalen Schwefel und möglicherweise auch dem Stickstoffkreislauf verknüpft sind (**Part 2 Report 2d**). Zur Analyse der Gemeinschaftsstruktur der Pseudo-nitzschia entlang des östlichen, süd-chinesischen Meeres wurden Amplifikation an insgesamt 75 Oberflächen-Wasserproben (gesammelt während der lokalen und SO218 - Ausfahrten) durchgeführt und die Amplifikate wurden durch Fragment-Analyse der DNA untersucht. So wurden insgesamt 50 Ribotypen nachgewiesen und so die Gemeinschaftsstruktur mit Hilfe genetischer Information (automated ribosomal intergenic spacer analysis, ARISA) identifiziert (**Part 2 Report 2b**).

Die Abteilung für schädliche Algenblüten (SABs) innerhalb des UMS Borneo marinen Forschungsinstituts (BMRI), führte Studien im Küstengewässer von Sabah durch, wo häufig und

wiederholt „rote Tiden“ vorkommen. Im Bezug auf dieses Thema sind die biogeographischen Ursprünge und phylogenetischen Beziehungen der „Cochlodinium polikrikoides“, aktuell die verursachende Art der SAB in Sabah und zudem jüngst in vielen anderen Regionen beschrieben von Interesse. Die Wasserqualität im offshore Bereich Sabahs wurde mit den küstennahen Resultaten verglichen. Die gewonnenen physikalischen Daten unterstützen die Ergebnisse vorangegangener Analysen zur Identifizierung der Herkunft der Wassermassen von der Westküste Sabahs und damit die laufende Forschung der Malaysia Sabah Universität und im Besonderen die des marinen Forschungsinstituts Borneo (**Part 2 Report 13**).

Da es ein Ziel der Untersuchungen war, die Bedeutung der ozeanischen Emissionen leichtflüchtiger Brom- und Jodverbindungen aus der untersuchten tropischen Region für die stratosphärische Halogenbelastung abzuschätzen wurde der **Transport der Emissionen** im tropischen Atlantik und West Pazifik **in die Stratosphäre** mit Hilfe des Trajektorienmodells FLEXPART untersucht (**Susann Tegtmeier, Kirstin Krüger, Birgit Quack**). Die Transportsimulationen, die das Auswaschen und den chemischer Zerfall der sehr kurzlebigen Halogenverbindungen berücksichtigen, basieren auf den Messungen der Brom- und Jod-Emissionen während der SHIVA SONNE SO218-Kampagne. Im Vergleich dazu wurden außerdem Messungen im tropischen Ostatlantik im Mai/Juni 2010 (DRIVE P399-Kampagne), und im tropischen Westpazifik im Oktober 2009 (TransBrom Sonne Kampagne) ausgewertet. Während in allen Regionen, einschließlich der mauretanischen Auftriebsregion im Ostatlantik, erhebliche VLSL Emissionen vom Ozean in die Atmosphäre beobachtet wurden, so ist der anschließende Transport von der Meeresoberfläche bis in die tropische Tropopausen-Schicht und die darüber liegende Stratosphäre im küstennahen West Pazifik am intensivsten. Die Evaluierung der drei tropischen Kampagnen zeigt, dass maximale Emissionen bromierter VLSL zusammen mit starken konvektivem Transport zu signifikanten VLSL Vorkommen in der Tropopausenregion führt, welches mit atmosphärischen in-situ Messungen gut übereinstimmt. Für Methyljodid allerdings sind die basierend auf den Emissionen berechneten atmosphärischen Vorkommen über dem tropischen Westpazifik höher als Beobachtungen basierend auf Flugzeug- und Ballonmessungen, die vor allem im Ostpazifik durchgeführt wurden. Dieser Vergleich deutet an, dass bisher existierende lokale in-situ Messungen in der Troposphäre und Stratosphäre möglicherweise nicht repräsentativ sind und Methyljodid einen größeren Einfluss auf die atmosphärische Ozonchemie haben könnte als bisher angenommen (**Anhang Report 14**).

## II.2. FÖRDERUNG UND ANGEMESSENHEIT DER ARBEIT

Im EU-geförderten Projekt SHIVA war ein Großteil der Mittel für die Durchführung der Seereise beantragt worden. Die im BMBF SHIVA-Sonne SO218 Antrag veranschlagten Kosten waren zusätzliche Ausgaben, die in dem EU- SHIVA-Vorhaben nicht berücksichtigt waren, und die durch die enge Zusammenarbeit mit Malaysia und den Philippinen entstanden. In stattfindenden Vorbesprechungen bekundeten Malaysier aller Provinzen deutlich ihr Interesse an der Kampagne und auch an der aktiven Datenauswertung. Es wurden daraufhin Bordplätze für 4 malaysische und 1 philippinischen Wissenschaftler angeboten, die zum Gelingen der Expedition beitrugen. Zusätzlich entstanden Reisekosten für einen malaysischen und einen philippinischen Militärbeobachter. Darüber hinaus wurde mit der Universität Kuala-Lumpur als ein malaysisches Kooperationsprojekt der Einsatz ihres 75khZ-ADCP zur Messung der Oberflächenmeeresströmungen vereinbart. Das Gerät wurde von einem malaysischen Techniker an Bord der Sonne in Singapur installiert und in Manila wieder deinstalliert. Die beteiligten Gruppen der vier malaysischen Universitäten benötigten insbesondere Reisegelder und Transportkosten, sowie einen kleinen Bedarf an Verbrauchsmaterial und Chemikalien. Einen weiteren großen Kostenpunkt stellten die Einsätze lokaler Boote zur küstennahen

Probenahme und zum Probentransport zu FS Sonne dar, da gerade an der Küste hohe Spurengaskonzentrationen und -emissionen erwartet und bestätigt wurden. FS Sonne konnte wegen des flachen Schelfgebietes nicht näher als 10 Seemeilen an die Küste heranfahren.

Arbeits-, Zeit- und Ausgabenplanung wurden eingehalten. Die vom BMBF zur Verfügung gestellten Mittel für die Kooperation mit den malaysischen und philippinischen Wissenschaftlern, darunter im wesentlichen Reisekosten der sieben auf FS Sonne beteiligten malaysischen und philippinischen Wissenschaftler und Beobachter, sowie einiger Aufbauhelfer, Einsatzkosten für drei örtliche Bootseinsätze (Kuching, Kota Kinabalu, Semporna - hier kein direkter Kontakt mit FS Sonne), sowie Transportkosten der an Bord gesammelten Proben und Geräterücktransporte zu den Heimatinstituten wurden bestimmungsgemäß und erfolgreich verwendet.

Im Rahmen der Schifffreise und der gesamten SHIVA-Kampagne wurde zur Zusammenarbeit von verschiedenen Gruppen und Disziplinen aufgerufen, um zum einen die Einmaligkeit der logistisch und administrativ aufwendigen Forschungsreise für die Spurengasfragestellungen zu nutzen und zum anderen die Zusammenarbeit mit den im EU-Projekt SHIVA beteiligten wissenschaftlichen Disziplinen zu verwirklichen. Die gemeinsame Expertise kann es ermöglichen Werkzeuge zu entwickeln, um die Ozean- und Atmosphärenflüsse der halogenierten Verbindungen zu parametrisieren und dadurch eventuell vorhersagbar zu machen. Diese wissenschaftlichen Produkte sind notwendig um den stratosphärischen Halogengehalt besser abschätzen zu können und damit die Ozonentwicklung im Rahmen zukünftiger Klimaänderungen und atmosphärischer Verschmutzung besser vorhersagen zu können.

Die Arbeiten, besonders die in diesem Forschungsvorhaben beantragen biologischen Arbeiten der malaysischen und philippinischen Wissenschaftler stellten eine hervorragende Ergänzung zu dem SHIVA-Projekt dar. Es wurden aus einem Gebiet, aus dem es bisher kaum Messungen gab, eine Vielzahl klimarelevanter Spurengase in Ozean und Atmosphäre gemessen und eine intensive Analyse der ozeanischen Biologie führe zur weiteren Aufdeckung von Quellen und ihre Einträge aus dem Ozean bis in die Troposphäre und Stratosphäre konnte berechnet werden.

Da die meisten Arbeiten erfolgreich verliefen und die meisten Daten ausgewertet sind und ein einmaliger Datensatz erhalten wurde, der in der Datenbank HalocAt und Datenbanken bei GEOMAR und der Universität Heidelberg, der wissenschaftlichen Gemeinschaft zur Verfügung gestellt werden kann die geleistete Arbeit als notwendig und angemessen gelten.

### **II.3. VERWERTBARKEIT DER ERGEBNISSE**

Das erreichte Ziel des Projektes war es, wissenschaftliche Informationen und Fachwissen zu globalen Umweltfragestellungen und Anpassungsmechanismen an den globalen Klimawandel zu liefern. Dies beinhaltet die Bereitstellung wissenschaftlicher Beiträge von öffentlichem Interesse zum internationalen SOLAS (Surface Ocean Lower Atmosphere Study)-Programm, an dem sich das BMBF mit der Förderung des Verbundprojektes SOPRAN (Surface Ocean Processes in the Anthropocene) beteiligt, in dem auch die Thematik der Ozeanemissionen halogener Verbindungen integriert ist.

Die Ergebnisse dienen der Stärkung der wissenschaftlichen Basis gesellschaftspolitisch relevanter Bewertungen und liefern Beiträge zum „WMO Ozone-Assessment“ und zu Fragen und Studien des IPCC (Intergovernmental Panel on Climate Change). Die internationalen Vereinbarungen zum Klimaschutz von Montreal (1989) über die Produktion ozonzerstörender Verbindungen und Kyoto (1997) zur Emissionsbegrenzung von Treibhausgasen, haben gezeigt, wie wichtig die Kenntnisse über die Emissionen von Spurengasen bei politischen Entscheidungen sind. Es könnte sich zukünftig



herausstellen, dass die globale Erwärmung und die dadurch zunehmende Temperatur des Ozeans und verstärkte Windgeschwindigkeiten zu einer verstärkten Emission ozeanischer Spurengase führt. Eine mögliche Zunahme von Konvektionsgebieten könnte einen bisher unterschätzten Beitrag zur Halogenchemie der Stratosphäre und damit zum Ozonabbau in Synergie mit den anthropogenen Chlorverbindungen leisten, was weitere Überlegungen beeinflussen würde.

In dem BMBF-Sonne Projekt fand eine Vernetzung bisher getrennter wissenschaftlicher Disziplinen statt, die zu einer Synergie der vorhandenen Expertisen führten, wie es in den internationalen Initiativen und Projekten SOLAS, SOPRAN, SPARC und CCMVal angedacht ist. Dies beinhaltet zusätzliches Fachwissen für eine Anpassung an den globalen Klimawandel, der zentral für die Aufgabenstellung des BMBF ist.

Um Effekte des globalen Wandels auf das empfindliche marine Ökosystem besser beschreiben zu können, müssen zunächst die existierenden Systeme besser verstanden werden. Ein solches Verständnis ist eine Grundvoraussetzung, um die Folgen anthropogener Einflüsse, einschließlich des Klimaschutzes, sowie Schutzes globaler Ökosysteme und mariner Ressourcen, vorhersagen und bewerten zu können. Es ermöglicht die Empfindlichkeit dieser entscheidenden Beziehungen des globalen Systems gegenüber veränderlichen Klimaeinflüssen beurteilen zu können, die für zahlreiche Aspekte der Klimaschutzbemühungen von Bedeutung sind.

Als ein Projektergebnis stehen unter anderem die ersten Daten einer Vielzahl von Spurengasen und weiterer Parameter aus einer wenig untersuchten Ozeanregion zur Verfügung. Die wissenschaftlichen Erfolge dieses Projektes schlagen sich im Wesentlichen in Veröffentlichungen in anerkannten und begutachteten wissenschaftlichen Zeitschriften nieder. Dieser einmalig kombinierte Datensatz, auch von verschiedenen Messplattformen aus, liefert die Grundlage für interdisziplinäre Veröffentlichungen, die zum Wissenschaftstransfer führen werden. In den Zeitschriften *Atmospheric Chemistry and Physics* und *Biogeosciences* wurde für diese Veröffentlichungen ein gemeinsamer Spezialband: *The EU Project SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere)* für Veröffentlichungen aus der SHIVA-Kampagne eingerichtet.

In den folgenden Jahren wird weiterhin an der Auswertung der Feldkampagnen gearbeitet, und die Themen und Partner während SO218 sind weiterhin ein integrativer Bestandteil neuer Projekte und werden weiterhin Grundlagen für zukünftige und innovative Projekte im Hinblick auf die schützende Ozonschicht und den Klimawandel liefern.

Während SO218 wurden aus dem Südchinesischen Meer und der Sulu-See wertvolle Erkenntnisse und erstmalige Daten für die Extrapolation lokaler Datensätze auf großräumige und globale Skalen erhalten. Die regional neuartigen Daten fließen in die Datenbank HalOcAt ([www.halocat.geomar.de](http://www.halocat.geomar.de)) ein, die im Rahmen der EU-COST (European Cooperation in the field of Scientific and Technical Research) ACTION 735: "Tools for Assessing Global Air–Sea Fluxes of Climate and Air Pollution Relevant Gases" als Teil des internationalen SOLAS initiiert wurde. Die während der Schiffskampagne gewonnenen Daten werden unter der Anwendung neuer wissenschaftlicher Erkenntnisse von Atmosphärendynamikern und Chemikern ausgewertet und stehen nach der Auswertung durch das SHIVA-Projekt der internationalen Gemeinschaft der Klimachemiemodellierer, CCMVal/ SPARC-Initiative) zur Verfügung. Die Datengrundlage für zukünftige Modellexperimente ist somit verbessert, die dadurch verbesserte Ergebnisse liefern können. Die Daten werden letztendlich in die vom AWI World Data Center for Marine Environmental Sciences (WDC-MARE) geführte internationale Datenbank PANGAEA (Publishing Network for Geoscientific & Environmental Data) eingetragen und stehen so der gesamten wissenschaftlichen Gemeinschaft zur Verfügung.

Mit Hilfe des erweiterten Datensatzes wird zum Beispiel im vom BMBF geförderten Projekt „Quellen und Senken bromierter und jodierter Verbindungen im tropischen Ozean“ innerhalb SOPRANs

(Surface Ocean Processes in the Anthropocene) in den kommenden zwei Jahren der Luft-Wassergasaustausch von bromierten und jodierten Verbindungen regional und global synthetisiert und simuliert. Mit der nationalen und internationalen atmosphärischen Wissenschaftsgemeinschaft ergaben sich neue Projekte, wie zum Beispiel das vom BMBF im Rahmen von ROMIC (Role Of the Middle atmosphere in Climate) kürzlich bewilligte Projekt „THREAT: The role of oceanic halogen and sulfur compounds for the middle atmosphere in a changing climate“, in dem bis 2016 gegenwärtige und zukünftige Ozeanemissionen und ihre atmosphärischen Transportwege und Eintragswege in die Stratosphäre eine bedeutende Rolle spielen. Die Erkenntnisse über Probenschema und Ergebnisse der Forschungsreise SHIVA-SONNE wurden für eine Seereise in das peruanische Auftriebsgebiet im Dezember 2012 in den östlichen Pazifik genutzt, aus dem nun auch zum ersten Mal Daten über Emissionen und Quellen kurzlebiger Halogenkohlenwasserstoffe vorliegen. In einem neuen BMBF-Projekt – eine Seereise mit FS Sonne in den indischen Ozean (OASIS) werden erstmalige Messungen dieser und weiterer Spurengase im zentralen indischen Ozean mit FS Sonne im Jahr 2014 durchgeführt. Die Erfahrungen mit den Projektpartnern der DLR und der malaysischen Institutionen können in den kommenden Jahren für weitere Projektplanungen genutzt werden.

Da es sich bei der Forschung auf dem Gebiet der halogenierten Spurengase, ihren Quellen und ihrem Transport in die Stratosphäre um ein aktives Forschungsgebiet handelt, auf dem weltweit jedoch nur relativ wenige Wissenschaftler arbeiten, sind während der Projektjahre weitere Publikationen über ozeanische Quellen der halogenierten Spurengase vorwiegend aus anderen Meeresregionen bekannt geworden. Ebenso wurden neue globale Modellansätze getestet, um Quellen, Transport und Eintrag der Spurengase in die Stratosphäre zu untersuchen. Ein Großteil der Arbeiten wurde von SHIVA-beteiligten Wissenschaftlern initiiert.

Die chlorierten, bromierten und jodierten kurzlebigen Verbindungen, die aus dem Ozean in die Atmosphäre gelangen sind sehr heterogen verteilt sind und ihr Eintrag in die Atmosphäre ist unter anderem von der Quellverteilung, der Wassertemperatur, der ozeanischen und atmosphärischen Schichtung und der Windgeschwindigkeit abhängig. Da die Einzelfaktoren und ihr Zusammenspiel bisher nur sehr unzureichend untersucht und verstanden ist, sind weitere Untersuchungen unabdingbar. Die in diesem Projekt gesammelten Daten liefern einen wichtigen Beitrag zum weiteren Verständnis des komplexen Systems. Die Heterogenität und Dynamik der Quellen sowie die lokalen bis hin zu globalen Bedeutungen dieser Spurenstoffe machen weitere Forschungen und Messkampagnen notwendig. Da ein Teil der Verbindungen, die auch in Spurenkonzentrationen große Auswirkungen auf die Atmosphäre haben können, durch anthropogene Aktivitäten beeinflusst wird, müssen die Beobachtung der Entwicklungen der ozeanischen Emissionen, sowie die anthropogenen und natürlichen Einflussfaktoren auch weiterhin im Fokus der Wissenschaftler bleiben. Auch durch die Abnahme des Beitrages der anthropogenen Fluorchlorkohlenwasserstoffe werden die marinen Emissionen der halogenierten Verbindungen für die Stratosphäre weiterhin an Bedeutung gewinnen.

Im Laufe der letzten Jahre wurden einige Veröffentlichungen zur Seereise und zur SHIVA-Kampagne in Spezialbänden einiger wissenschaftlicher Zeitschriften publiziert und weitere sind in Vorbereitung. Die Daten und Ergebnisse wurden bei nationalen und internationalen Konferenzen auf Postern und in Vorträgen präsentiert. Diese Veröffentlichungen finden sich im englischsprachigen Part 2 dieses Berichtes.



## Part 2: SO218- SHIVA English reports

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### RV SONNE CRUISE SO218: SINGAPORE-MANILA, 15-29 NOVEMBER 2011

Within the frame work of the EU-project SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) the research cruise SO218 of the German research vessel SONNE was organized and conducted by the Leibniz-Institute of Marine Sciences (IFM-GEOMAR, <http://www.ifm-geomar.de/>, now GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel, <http://www.geomar.de/>) from 15. to 29. November 2011 in the South China Sea and Sulu Sea. The RV Sonne (cruise SO218) sailed from Singapore to the Philippines following a track along the coast of Borneo and through the Sulu Sea (Figure 1). The route incorporated 2 diurnal stations off the western coast of Borneo, 2 contacts with local boats from the universities in Kuching and Kota Kinabalu, and was overflown by the GERMAN research air craft Falcon from the DLR German Aerospace Center on three occasions. The cruise was mainly bound to investigate trace gas emissions in waters of various biogeochemical regimes of the West Pacific and their contribution to stratospheric halogens. Partners on board were from the European project SHIVA - Stratospheric halogens in a varying atmosphere - (<http://shiva.iup.uni-heidelberg.de/>) and from Malaysia, the University of Malaya, Kuala-Lumpur (IOES) Universiti of Malaya, Sarawak (UNIMAS), Universiti of Malaya, Sabah (UMS) and the University of the Philippines Diliman, Quezon. During SO218, the first halocarbon measurements in waters of the coastal western Pacific were performed. Halocarbon concentrations were determined in water and air, and sea-to-air fluxes were calculated. Many other atmospheric trace gases, transport processes and various oceanic chemical, physical and biological parameters were also investigated.

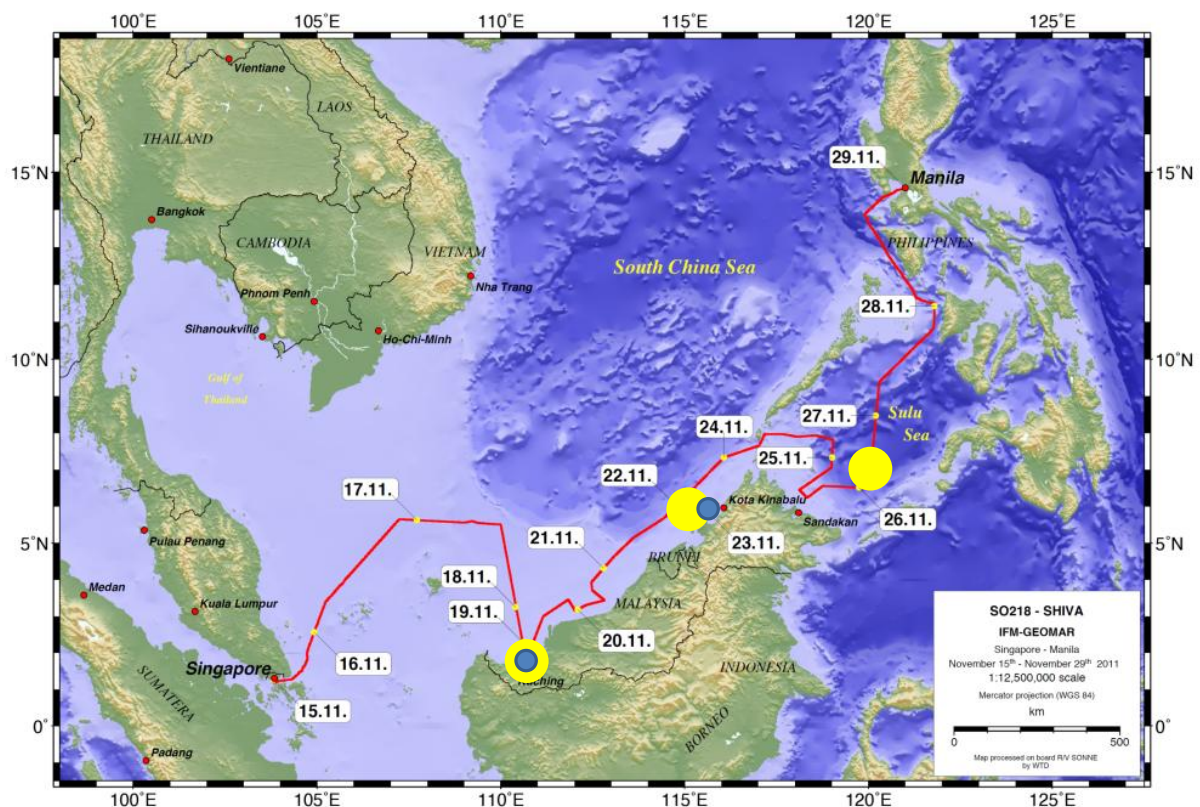


Figure 1: SO218-cruise track of RV Sonne: Singapore-Manila (15-29 November 2011), including the local boat meetings at Kuching and Kota Kinabalu (blue circles) and overflights by the DLR aircraft Falcon (yellow circles).

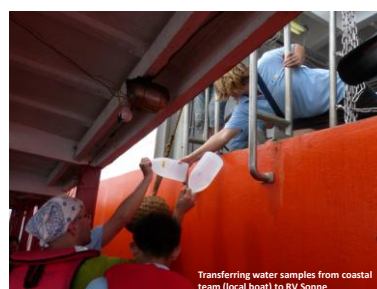
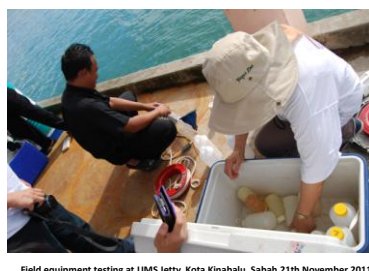


Figure 2: Impressions from the local boat deployments at Kuching, with additional deployment of deployment of Falcon and local cruise at Kota Kinabalu.

## SCIENTIFIC BACKGROUND

Trace gases, containing halogens as chlorine and bromine are broken down by solar radiation in the stratosphere, where the halogens are highly efficient at destroying ozone. Increasing emissions from human activities have led to depletion of global stratospheric ozone over the last three decades. Whereas the chlorine supply is dominated by anthropogenic compounds, a major part of the bromine is supplied by natural, short-lived species, with oceanic sources. The tropical oceans are a known source of reactive bromine and iodine to the atmosphere in the form of short-lived brominated and iodinated methanes as e.g. bromoform ( $\text{CHBr}_3$ ). Elevated atmospheric concentrations above the oceans are related to oceanic supersaturations of the compounds, and to natural photochemical and biological production. Macro algae in coastal regions, as well as regionally enhanced phytoplankton, river outflow, photochemical reactions and local anthropogenic sources all contribute to marine and atmospheric concentrations.

Trace gases enter the stratosphere principally in the tropics, where ascending warm air carries them rapidly upwards. The intense vertical transport of the tropical atmosphere implies that the oceanic sources could supply significant amounts of halogens to the upper troposphere/ lower stratosphere where they contribute to the observed ozone destruction. The tropical western Pacific is a largely uncharacterized region for the oceanic compounds and a projected hot spot, especially in coastal regions for their emissions and transport pathways into the stratosphere.

Spatial and temporal variability in production and sea-to-air flux of the short-lived halogenated trace gases create strong varying marine and atmospheric distributions and thus also varying stratospheric contributions. The current impact of the natural ozone depleting substances is still uncertain and future changes in the mechanisms, that regulate their emissions to the atmosphere, their transport, and their chemical processing became just object of current studies. The oceanic emissions have the potential to cause surprises in the future evolution of the ozone layer in a changing climate, unless they are better understood. The measurements in this study were needed to improve the present and future understanding of the stratospheric halogen loading and therewith ozone depletion. The results of the SHIVA-SONNE campaign contribute to the scientific underpinning of the United Nations Montreal Protocol on Substances that Deplete the Ozone Layer, to the United Nations Framework Convention on Climate Change, and to global climate change research.

## OBJECTIVES, PARTICIPATING INSTITUTIONS AND MEASUREMENTS

Of particular relevance during SO218 were oceanic and atmospheric measurements of a suite of short-lived trace gases containing the halogens chlorine, bromine and iodine in various marine biogeochemical regimes, as close to the coasts, in regions of high chlorophyll, close to coral reefs, in oceanic upwelling regions and in river outflows, compared to more open oceanic conditions and under differing meteorological conditions. From these measurements the climate-sensitive oceanic emission strengths and contributions of the emissions to stratospheric halogens are characterized by modeling.

The atmospheric structure was determined by intense radio and ozone soundings during the cruise. Other marine trace gases as i.e. nitrous oxide ( $\text{N}_2\text{O}$ ), dimethylsulfide (DMS), oxygen ( $\text{O}_2$ ) and carbon dioxide ( $\text{CO}_2$ ), were investigated as well. In situ and satellite measurements of phytoplankton groups, obtained by special retrieval methods from the SCIAMACHY and GOME-2 instruments gave further information about biogeochemical conditions during the ship expedition. Atmospheric concentrations of a variety of long-lived anthropogenic and natural trace gases were also determined. These measurements helped to identify transport pathways of the marine trace gases towards and away from the ship. The measurements on RV SONNE in the South China Sea and along the coastline of Peninsula Malaysia and Borneo in conjunction with Malaysian research partners were accompanied by



parallel measurements with the DLR Falcon and land-based investigation teams (see: The SHIVA Western Pacific campaign in November and December 2011, Post-campaign Activity Report by Pfeilsticker, 2012 and the SHIVA Final Report, <http://shiva.iup.uni-heidelberg.de>).

The instruments on board of the ship carried out quasi-continuous measurements of VSLS and related species in both seawater and air to determine actual sea to air fluxes, whilst the aircraft carried out surveys of the larger scale concentrations in the marine boundary layer and in the convective outflow at altitudes up to ~13 km.

Together with the main scientific objective of the cruise to characterize the oceanic emissions of natural halogenated gases in the tropical western Pacific, the participating groups also followed additional research questions. Thus, more specifically, the overall scientific program of SO218 included the following themes, which could roughly be assorted to individual working groups (Table 1):

- 1.) HALOCARBONS: Atmospheric and oceanic concentrations of bromine, iodine and chlorine containing halocarbons, in order to derive their sea to air fluxes.
- 2.) PHYTO-OPTICS and PLANKTON: Phytoplankton pigments, species and size distribution, radiation and absorption spectra of seawater and plankton content in order to characterize the phytoplankton and zooplankton composition and to validate satellite data from the western Pacific.
- 3.) OCEANIC TRACE GASES: Oceanic concentrations of dimethyl sulfide and related compounds (DMS, DMSO, DMSP), nitrous oxide and methane, in order to understand their distribution in the different biogeochemical regimes of the western Pacific and to gain new insights into halocarbon sources.
- 4.) OCEANSENSORS: Identification of carbon dioxide and oxygen sources and sinks; separation of physical and biological factors for observed sources and sinks, temperature and salinity.
- 5.) RADIOSOUNDING: Identification of meteorological vertical and ozone profiles in order to evaluate the mixing layer and tropopause height and to improve air mass back trajectories calculations to identify origin of sampled air masses. Finally, to validate chemical transport model results and the distribution of ozone above the western Pacific.
- 6.) AIRSAMPLING: Determination of anthropogenic and natural trace gas concentrations by flask sampling, to identify regional and diurnal gradients of some compounds and for intercalibration of different instruments.
- 7.) SPECTROSCOPY: Identification of reactive trace gases BrO and IO with Multi-Axis Differential Optical Absorption Spectroscopy (MAX DOAS) in a three dimensional field and Cavity Ring Down Spectroscopy as possible decomposition products of organic trace gases and for validation of satellite-data.
- 8.)  $\mu$ -DIRAC: Quasi-continuous measurements of some VSLS in the marine atmospheric boundary layer (15 m altitude) for real time concentrations.
- 9.) ATMOSPHERIC TRACE GASES: Continuous measurements of the atmospheric mixing ratios of a suite of pollution indicators and greenhouse gases (CO, CH<sub>4</sub>, O<sub>3</sub>, CO<sub>2</sub>) in order to investigate their spatial and temporal variability in the lower tropical marine boundary layer.
- 10.) CIMS-REACTIVE COMPOUNDS: Continuous measurements of Br<sub>2</sub>, BrCl, HOBr, BrO, and ClNO<sub>2</sub> and HNO<sub>3</sub>, HCl, SO<sub>2</sub>, and HBr in the marine boundary layer with two Atmospheric Chemical Ionization Mass Spectrometers, a LIF Instrument for IO and a NO<sub>x</sub> detector, which were deployed inside a specifically designed 10 ft container on the forecastle deck of the ship.

- 11.)ATMOSPHERIC AEROSOL: Major ions and halogens in aerosol samples, in order to identify their sources and quantify the halogen budget in the western Pacific atmosphere.
- 12.)OCEAN CIRCULATION: Ocean surface currents and transient tracers for age determination.
- 13.)LOCAL BOAT DEPLOYMENTS: Local boats visited the RV Sonne from our Malaysian partners (University of Malaysia-Sarawak) at Kuching on 19th November 2011 at noon and the University of Malaysia, Sabah at Kota-Kinabalu on 22nd November 2011.
- 14.)TRANSPORT INTO THE STRATOSPHERE: The halogen contribution of the local oceanic emissions to the upper tropospheric and lower stratospheric halogen content were calculated with the Lagrangian transport model FLEXPART.

Table 1: **SCIENTIFIC GROUPS. PARTICIPATING INSTITUTIONS AND CONTACTS:**

	Principal Investigator (PI)	groupno.+ name	Last Name	Fore Name	Function	University
	Ship					
			Quack	Birgit	chief scientist	IFM-GEOMAR
			Sapii	Mohamad Zaid bin	observer	NHD-Malaysia
			Magura	Benjamin Z. Magura	observer	Navy-Philippines
in water	Quack	1a: Halocarbons MS	Hepach	Helmke	student	IFM-GEOMAR
			Raimund	Stefan	technician	IFM-GEOMAR
	Wallace	1b: Halocarbons ED	Qiang	Shi	student	IFM-GEOMAR
	Bracher	2a: Biology; Pigments	Altenburg Soppa	Mariana	scientist	AWI- BREMERHAVEN
			Wiegmann	Sonja	technician	AWI- BREMERHAVEN
			Cheah	Wee	scientist	AWI- BREMERHAVEN
	UMUNIMAS	2b: Biology, speciation	Idid	Rizman	scientist	Universiti Malaya Kuala Lumpur
			Muhajid	Aazani	scientist	University Malaysia Sarawak
	Palermo		Palermo	Joseph	scientist	University of the Philippines Diliman
	Marandino	3a: OVO, C	Zindler	Cathleen	student	IFM-GEOMAR
	Quack	3b: Ox, Nuts	Marandino	Christa	student	IFM-GEOMAR
in air	Bange	3c: N <sub>2</sub> O, CH <sub>4</sub> , DMS				
	Körtzinger/Tanhu	4: P <sub>CO2</sub> , P <sub>O2</sub> , S,T	Schneider	Anke	scientist	IFM-GEOMAR
	Krüger	5: radiosonding	Krüger	Kirstin	scientist	IFM-GEOMAR
			Bieligk	Henner	scientist	IFM-GEOMAR
			Fuhlbrügge	Steffen	student	IFM-GEOMAR
	Atlas	6: air sampling	Wittke	Franziska	scientist	IFM-GEOMAR
	Pfeilsticker	7: CE- DOAS	Lampel	Johannes	student	Uni Heidelberg
	Harris/ Kreher	8: µ- DIRAC	Kinzel	Julian	scientist	Cambridge/IFM-GEOMAR
	Schlager	9: CO, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub>	Sentian	Justin	scientist	University Malaysia Sabah
			Abdullah	Nur Aleesha	scientist	Malaysian Meteorological Dep.
	Voigt	10a: CIMS, Br	Jurkat	Tina	student	DLR
			Schäuble	Dominik	scietist	DLR
	Heard	10b: IO, OH, Hox	Ingham	Trevor	scientist	Uni Leeds
	Hofmann		Bunyan	Hannah	student	Uni Leeds
	Baker	11: Aerosol				UEA-Norwich

AWI BREMERHAVEN

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## WORK PROGRAM DURING THE CRUISE

During the SO218 cruise of 'RV Sonne' from 15 to 29 November 2011 in the South China and Sulu Seas between Singapore and Manila (Philippines) a variety of chemical and physical parameters within the surface waters as well as between the atmospheric boundary layer and the stratosphere have been examined with different measurement frequencies. Data and samples were obtained using a variety of analytical instruments and sampling devices (Tables 1 and 2).

Table 2: Installed and operating instruments on board (Singapore-Manila; 15.-29. November 2011)

	Group	Instrument	Parameter
1	Halocarbons	Agilent GC/MS	iodinated, brominated and chlorinated VSLS
2	Halocarbons	Fisons GC 8000	iodinated, brominated and chlorinated VSLS
3	Phytoplankton/AWI	Pigments/Filtration	phytoplankton pigments, chl <sub>a</sub> 3, chl <sub>a</sub> 1+2,
4		Flowcytometry	phytoplankton size classes
5		Remote sensing (chl <sub>a</sub> maps)	phytoplankton speciation
6		FRRF_Fluorometer	chl <sub>a</sub>
7		Peristaltik/Pump	water supply
8		Microscopy	phytoplankton species
9	Radiation	RAMSES/ Container top	Radiane/Irradiance
10		RAMSES/ Monkey deck	Radiane/Irradiance
11		Fasttracka/ CTD	Radiane/Irradiance
12	Phytoplankton/Malaysia	UW Phyt. + Bacteria / Filter (150L water)	molecular characterization
13		CTD Phyt. + Bacteria / Filter (150L water)	zooplankton
14		Bongo Net/Plankton Net	zooplankton
15	Phytoplankton/Philippines	Infinity ME/ station/ fluorescence	phytoplankton
16	OVOC	GC/ MS	acetone, acetaldehyde, propanal, butanal, butanon
17		CDOM	humic acids
18	DMS	GC	DMS, DMSO, DMS
19	Ox/Nuts	Oxygen	CTD- discrete Winkler Oxygen
20		Nutrients	NO <sup>3-</sup> , PO <sub>4</sub> <sup>3-</sup> ,
21		N <sub>2</sub> O; CH <sub>4</sub>	nitrous oxide, methane
22	Tracer	Freon samples	CFC water age
23	PCO <sub>2</sub>	PCO <sub>2</sub>	CO <sub>2</sub> pressure in seawater
24		PO <sub>2</sub> (Oxygen optode)	Oxygen in Seawater
25		T	SST from Optode
26		Gas tension device	Total gas pressure in water
27	CTD	CTD	Temperature and Salinity profiles
28		Rosette sampler	water depth samples
29		Fluorometer	chlorophyll
30	Thermosalinograph	T/S	Temperature and Salinity continuous
31		meteorology	air temp, humidity, wind speed and direction,
32	Hydrographic shaft	CTD	temperature and salinity continuous
33		ADCP	ocean surface currents
34		sun-Pump	water samples from 4m depth
35		lowara	water samples from 4m depth
36	Radiosounding	Radiosondes	air temp, humidity, wind speed and direction profiles
37		Disdrometer	rain dropsizes
38		Rainsensor (Rudolph IRSS88)	rain
39		Ozon- sondes	ozone profiles
40	Air- sampling	Atlas flasks	> 50 trace gases, hydro-, halocarbons, freons, alkylnitra
41		Baker Aerosol	aerosol bromine, iodine speciation
42	Max Doas	Max Doas HD /Spectrometer (Acton)	BrO, IO
43		Max Doas HB/Spektrometer Shamrock 303i	BrO, IO,
44		Cavity HD	IO
45	μ-dirac	GC	CHBr <sub>3</sub> , CH <sub>2</sub> Br <sub>2</sub> , and chlorinated compounds
46	DLR	cavity ring down (CO <sub>2</sub> , CH <sub>4</sub> ,H <sub>2</sub> O)	CH <sub>4</sub> , CO <sub>2</sub> ; O <sub>3</sub> ; CO
47		UV-absorp., VUV-fluoresc. (CO/O <sub>3</sub> )	carbon monoxide, ozone
48		CIMS1(BrO, Br <sub>2</sub> , HOBr)	Br, HBr, BrO
49		CIMS2 (SO <sub>2</sub> ,HCl, HBr)	SO <sub>2</sub> ,HCl, HBr, nitril chloride
50	Leeds	LIF (IO)	IO
51		Nox-Box (NO <sub>2</sub> )	nitrous oxide
52		Denuder-Hofmann (I <sub>2</sub> )	I <sub>2</sub>



Regular water samples were collected from pump supplies submersed in the hydrographic shaft of the ship. Depth profiles were undertaken at selected locations to investigate the vertical hydrographic structure of the water column and to obtain trace gas profiles. Deep profiles of anthropogenic tracers were determined in the Sulu Sea to determine the water mass age. Several VSLs from sea water and air were analyzed directly on board the ship.

**Table 3:** Underway work plan and sampling strategy on board FS Sonne during SO218- SHIVA ( Group numbers ( refer to Table 1).

Zeit	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Gruppe																								
1	w/a	W	W	S	W	W	w/a	W	W	S	W	W	w/a	W	W	S	W	W	w/a	W	W	S	W	W
2	W	C	C	C	C	C	C	W	C	C	C	C	C	W	C	C	C	C	C	W	C	C	C	W
3		W			W			W			W			W			W			W				W
4	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
5	r						r						r/w/o						r					
6	(a)	(a)	(a)	(a)	(a)	(a)	a	(a)	(a)	(a)	(a)	(a)	a	(a)	(a)	(a)	(a)	(a)	2a	(a)	(a)	(a)	(a)	(a)
7	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
8	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
9	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
10	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C

w: water sample  
a: air sample (occasional)  
c: continuous  
r: radio sonde  
o: ozone sonde  
st: standard

The working schedule during transit included continuous sampling of seawater, a collection of discrete air samples, the installation of optical measuring techniques and the uplift of research balloons. During the cruise samples have been obtained with 52 instruments and sampling devices (Table 2). Routinely hourly to three hourly water and - air samples have been taken from pump supplies submersed in the hydrographic shaft, respectively installed on the monkey deck (Work Groups 1, 2, 3, 4, 6). Meteorologists sent weather balloons with physical and O<sub>3</sub>-sondes to the stratosphere (up to 30 km height) every six hours (Work Group 5), with an increased frequency of two hours on the two diurnal stations on 18./19<sup>th</sup> and 21./22<sup>nd</sup> November, which were conducted in open waters each roughly 60 nm off-coast from Kuching and Kota-Kinabalu and an increased frequency was also performed on the North East coast off Borneo on 25<sup>th</sup> November 2011.

After these stations, boats from our Malaysian partners at Kuching from the University of Malaysia-Sarawak on 19<sup>th</sup> November at noon, at Kota-Kinabalu from the University of Malaysia, Sabah on 22<sup>nd</sup> November visited the RV Sonne. During these local ship cruises, water samples were taken (at 1 km, 5 km, 10 km, 15 km, and 20 km off-coast) and exchanged with samples taken in the open ocean by the



Figure 3: Meetings and simultaneous measurements of RV SONNE and DLR aircraft Falcon – stationed in Miri on Borneo during the SHIVA campaign- were and performed on 19<sup>th</sup> November, 12 LT and on 21<sup>st</sup> November, 11 LT (photo: Torsten Bierstedt).

RV Sonne team. The local boat water samples were analyzed for their content of trace gases and phytoplankton on board RV Sonne. Open ocean measurements were thus complemented by near shore and coastal gradients from the local ships and atmospheric measurements through the troposphere by the aircraft Falcon, starting at the same height of 15m above sea level as air samples were taken on board of RV Sonne.

The optical sensors and continuous instruments have been installed in the beginning of the cruise on the monkey deck, the bow and in a research container (Work Groups 3, 7, 8, 9, 10).

Various halogenated hydrocarbons have been analyzed directly on board using a gaschromatography/mass spectrometry system (Work Group 1). Oxygenated trace gases and dimethyl sulfide were also analyzed directly with a gas chromatograph/mass-spectrometric system from sea water (Work Group 3), while carbon dioxide and oxygen were measured immediately with sensors within the upper oceanic layer (Work Group 4). More trace gases in sea water ( $N_2O$ ,  $CH_4$ ) were analyzed by gas chromatography post-cruise in the laboratory (Work Group 3). Biological sampling included parameters of organic carbon and nitrogen as well as pigments, the amount and sizes of cells and the composition and activity of the phytoplankton and zooplankton (Work Group 2). The optical properties of seawater and its ingredients were measured as reference spectra for the validation of satellite data analysis, in order to detect the composition, distribution and productivity of phytoplankton (Work Group 2).

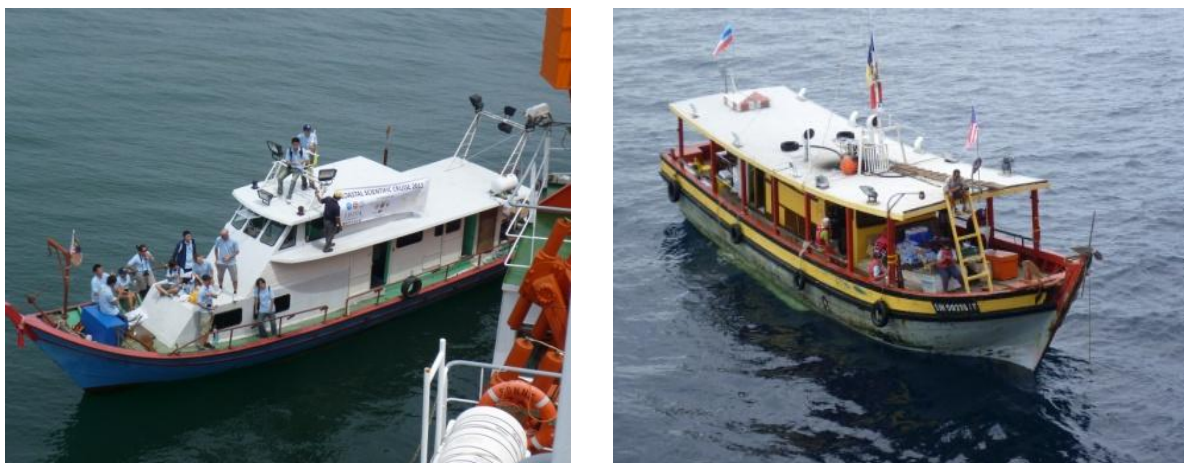


Figure 4: Local boats visited the RV Sonne from our Malaysian partners (University of Malaysia-Sarawak) at Kuching on 19<sup>th</sup> November at noon and the University of Malaysia, Sabah at Kota-Kinabalu on 22<sup>nd</sup> November 2011.

Discrete air samples were taken for partners of the Universities Norwich (15 samples) as well as the 'Rosenstiel School of Marine and Atmospheric Sciences' in Miami (200 samples) (Work Groups 6, 11). In the respective home laboratories more than 70 anthropogenic and natural trace gases, and elements in aerosols within the marine boundary layer were analyzed following the cruise. Atmospheric profiles of temperature, humidity and different kinds of trace gases (e.g. ozone, nitric oxide, bromine oxide, carbon monoxide) were examined on the basis of optical measurements, by rises of research balloons and mass spectrometers (Work Groups 5, 6, 8, 9, 10).

The analysis of the extensive dataset from the ocean and the atmosphere collected during SO218 brought new insights into the interaction of ocean and atmosphere. The results were presented at international conferences (SOLAS, EGU and AGU conferences) and first publications already appeared in the SHIVA- special issue of the peer reviewed scientific journals *Atmospheric Chemistry and Physics* and *Biogeosciences* (Table 4).



Figure 5: Release of an ozone-sonde at night (photo: Johannes Lampel).

Table 4: **PUBLISHED ARTICLES, PUBLICATIONS IN PROGRESS AND PRESENTATIONS AT NATIONAL AND INTERNATIONAL CONFERENCES**

Articles

1. Bracher, A., Cheah, W., Dinter, T., Steinmetz, F. Deriving phytoplankton characteristics from optical properties in the South China Sea and Sulu Sea, in prep for Ocean Sciences.
2. Cheah W., et al., Photophysiological state of natural phytoplankton communities in the South China Sea and Sulu Sea, *Biogeosciences Discussion* 10:12115-12153, 2013.
3. Fuhlbrügge et al., Exchange of VSLs in the marine boundary layer with the free troposphere during SHIVA-SONNE, *ACPD* (in prep.), 2013.
4. Hamer, P. D., Marécal, V., Hossaini, R., Pirre, M., Warwick, N., Chipperfield, M., Samah, A. A., Harris, N., Robinson, A., Quack, B., Engel, A., Krüger, K., Atlas, E., Subramaniam, K., Oram, D., Leedham, E., Mills, G., Pfeilsticker, K., Sala, S., Keber, T., Bönisch, H., Peng, L. K., Nadzir, M. S. M., Lim, P. T., Mujahid, A., Anton, A., Schlager, H., Catoire, V., Krysztofiak, G., Fühlbrügge, S., Dorf, M., and Sturges, W. T.: Modelling the chemistry and transport of bromoform within a sea breeze driven convective system during the SHIVA Campaign, *Atmos. Chem. Phys. Discuss.*, 13, 20611-20676, doi:10.5194/acpd-13-20611-2013, 2013.
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10. Huang, Peng, Tanhua, T., Ventilation and anthropogenic carbon in the Sulu Sea, in prep.
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12. Raimund, S. et al., Oceanic sources of VSLs in the South China and Sulu Seas, in prep.
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  18. Ziska, F., Quack, B., Abrahamsson, K., Archer, S., Atlas, E., Bell, T., Butler, J., Carpenter, L., Jones, C., Harris, N., Hepach, H., Heumann, K., Hughes, C., Kuss, J., Krüger, K., Liss, P., Moore, R.M., Orlikowska, A., Raimund, S., Reeves, C., Reifenhäuser, W., Robinson, A., Schall, C., Tanhua, T., Tegtmeier, S., S. Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S., Yokouchi, Y., Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, *Atmos. Chem. Phys. Discuss.*, 13, 5601-5648, doi:10.5194/acpd-13-5601-2013, 2013.
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#### Presentations (poster and talks)

1. Cheah, W., Taylor, B., Dinter, T., Wiegmann, S., Altenburg-Soppa, M., Palermo, J., Bracher, A., Composition and optical features of phytoplankton during SHIVA-SONNE (SO218) expedition, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster, 2013.
2. Cheah W., Taylor B., Dinter T., Raimund S., Quack B., Bracher A., Community structure and optical properties of phytoplankton during SHIVA-Sonne expedition: From in-situ and satellite. South China Sea Conference 2012, 22 - 26 October 2012 Kuala Lumpur, Malaysia, Talk, 2013.
3. Fuhlbrügge, S., Krüger, K., Quack, B. und das SHIVA SONNE Team, SHIVA SONNE SO218: Analysis of meteorology and air masses, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster, 2013.
4. Fuhlbrügge, S., Quack, B., Tegtmeier, S., Atlas, E., Sala, S., Boenisch H., Hepach, H., Raimund S., Shi Q., Krüger, K.; Exchange of VSLs in the marine boundary layer with the free troposphere during SHIVA-SONNE, EGU General Assembly, Vienna, Poster, 2013
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7. Krüger, K., Does the ocean impact the ozone layer?", (invited) Kyushu Universität, Fukuoka, 6. March 2013.
8. Krüger, K., The TransBrom Sonne expedition in the tropical West Pacific: from Tomakomai (Japan) to Townsville (Australia) during October 2009 (invited), JAMSTEC, Yokohama, Japan, 20 February 2012
9. Krüger Kirstin, "Ocean-stratosphere interactions in a changing climate", UiO, Oslo, 22. November 2012, (invited) Talk, 2012.

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12. Kuek, F.W.I., Ngu, E.S.L., Lee, S.T.H., Mujahid, A., Lim, P-T., Leaw,C-P., Müller, M. , Microbial communities of the Eastern South China Sea and Sulu Sea and their possible roles in the DMS(P) cycle, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster, 2013.
13. Lampel, J., Wittrock, F., Großmann, K., Peters, E., Horbanski, M., Pöhler, D., Frieß, U., Pfeilsticker, K., Platt, U., DOAS measurements from space, ship and plane: trace gas distributions over the South China and Sulu Sea, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster, 2013.
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In the following, **SHORT REPORTS FROM THE PARTICIPATING INSTITUTIONS** are presented which give an insight into their objectives, methods and results.

**Theme 1 - HALOCARBONS:** Atmospheric and oceanic concentrations of bromine, iodine and chlorine containing halocarbons.

**Report 1:** *Halocarbons in the South China and Sulu Sea: distributions emissions and sources*, Birgit Quack, Helmke Hepach, Stefan Raimund, Qiang Shi, Wee Cheah, Astrid Bracher

**Theme 2 - PHYTO-OPTICS and PLANKTON:** Phytoplankton pigments, species and size distribution, radiation and absorption spectra of seawater and plankton content

**Report 2a:** *Natural phytoplankton communities and optical properties of phytoplankton during SHIVA-Sonne expedition in November 2011 in the South China Sea and Sulu Sea, Infinity ME*, Astrid Bracher, Wee Cheah, Sonja Wiegmann, Mariana Altenburg-Soppa, Joseph Dominic Palermo, Birgit Quack, Stefan Raimund, Gerd Krahmann

**Report 2b:** *Community structure of Pseudo-nitzschia (Bacillariophyceae) from the SHIVA expedition*, Sing-Tung Ten, Po-Teen Lim, Hong-Chang Lim, Aazani Mujahid, Chui-Pin Lea

**Report 2c:** *Microbial communities of the eastern South China Sea and the Celebes Sea and their possible roles in the DMS(P) Cycle*, Felicity W.I. Kuek, Aazani Mujahid, Moritz Müller

**Report 2d:** *Culturable bacteria from Talang-Talang Reef and its surrounding waters*, Felicity W.I. Kuek, Lin-Hui Ngu, Li-Fang Lim, Aazani Mujahid, Moritz Müller

**Theme 3 - OCEANIC TRACE GASES:** Oceanic concentrations of dimethyl sulfide and related compounds (DMS, DMSO, DMSP), nitrous oxide and methane

**Report 3:** *Interaction of climate active gases during the SHIVA-Sonne SO218 campaign: Dimethylsulfide, oxygenated volatile organic compounds, nitrous oxide (N<sub>2</sub>O), and methane (CH<sub>4</sub>)*, Christa Marandino, Cathleen Zindler, Hermann W. Bange, and Franziska Ziska

**Theme 4 – OCEAN SENSORS:** Identification of carbon dioxide and oxygen sources and sinks; separation of physical and biological factors for observed sources and sinks, temperature and salinity

**Report 4:** *Underway measurements of pCO<sub>2</sub>, oxygen and total gas pressure*, Tobias Steinhoff, Anke Schneider and Arne Körtzinger

**Theme 5 - RADIOSOUNDING:** Identification of meteorological vertical and ozone profiles in order to evaluate the mixing layer and tropopause height and to calculate air mass back trajectories

**Report 5:** *SHIVA SONNE SO218: Radio- and Ozonesounding*, Kirstin Krüger, Steffen Fuhlbrügge, Henner Bieligk

**Theme 6 – AIR SAMPLING:** Determination of anthropogenic and natural trace gas concentrations by flask sampling

**Report 6:** *Determination of trace gas concentrations in the marine boundary layer*, Elliot Atlas, Steffen Fuhlbrügge, Kirstin Krüger, Birgit Quack

**Theme 7 - SPECTROSCOPY:** Identification of reactive trace gases BrO and IO with Multi-Axis Differential Optical Absorption Spectroscopy (MAX DOAS) in a three dimensional field and Cavity Ring Down

**Report 7:** *Trace Gas Measurements using MAX-DOAS and CE-DOAS instruments*, Johannes Lampel, Folkart Wittrock

**Theme 8 -  $\mu$ -DIRAC:** Quasi-continuous measurements of some VSLS in the marine atmospheric boundary layer (15 m altitude) for real time concentrations

Report 8:  *$\mu$ -Dirac – continuous measurements of halogenated trace gases*, Neill Harris, Andrew Robinson, Karin Kreher, Elliot Atlas, Julian Kinzel, Birgit Quack

**Theme 9 – ATMOSPHERIC TRACE GASES:** Continuous measurements of the atmospheric mixing ratios of a suite of pollution indicators and greenhouse gases (CO, CH<sub>4</sub>, O<sub>3</sub>, CO<sub>2</sub>)

Report 9: *Atmospheric CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, O<sub>3</sub> and CO (DLR- Instrumentation)*, Hans Schlager, Justin Sentian, Nur Aleesha Abdullah.

**Theme 10 - CIMS-REACTIVE COMPOUNDS:** Continuous measurements of Br<sub>2</sub>, BrCl, HOBr, BrO, and ClNO<sub>2</sub> and HNO<sub>3</sub>, HCl, SO<sub>2</sub>, and HBr in the marine boundary layer with two Atmospheric Chemical Ionization Mass Spectrometers, a LIF Instrument for IO and a NO<sub>x</sub> detector

Report 10a: *DLR- CIMS measurements: Investigation of anthropogenic emissions affecting air quality in the marine boundary layer of the South China and Sulu Sea*, Tina Jurkat, Christiane Voigt, Dominik Schäuble

Report 10b: *Sonne-Falcon Lagrangian tracer experiment and continuous carbon monoxide and ozone measurements*, Hans Schlager, Yu Ren, Michael Lichtenstern, Monika Scheibe, Nur Aleesha Abdullah, Justin Sentian, Tina Jurkat, Dominik Schäuble

Report 10c: *In situ measurements of IO by Laser-Induced Fluorescence Spectroscopy*, Hannah Walker, Trevor Ingham, Dwayne Heard

Report 10d: *Measurements of I<sub>2</sub> and the sum of HOI + ICl during SHIVA*, Hannah Walker, Trevor Ingham, Dwayne Heard, Ru-Jin Huang, Thorsten Hoffmann

**Theme 11 - ATMOSPHERIC AEROSOL:** Major ions and halogens in aerosols

Report 11: *Aerosol chemistry of halogens during SHIVA*, Alex Baker and Chan Yodle,

**Theme 12 – OCEANIC SURFACE CURRENTS**

Report 12: *Oceanic Circulation -Transient tracer measurements during cruise Sonne-218*, Toste Tanhua, Peng Huang, Anke Schneider

**Theme 13 – LOCAL BOAT DEPLOYMENTS**

Report 13a: *Results of the local boat deployments Kuching, Kota Kina Balu, and Semporna*  
Felicity W.I. Kuek, Aazani Mujahid, Lim Po Teen, Leaw Chui Pin, Moritz Müller, Ann Anton

Report 13b: *Results of the local boat deployment Kuching*, Moritz Müller, Aazani Mujahid, Felicity W.I Kuek, Hong-Chang Lim, Sing-Tung Teng, Chui-Pin Leaw, Ann Anton, Lim Po Teen

Report 13c: *Results of the local boat deployment Kota Kinabalu*, Ann Anton

**Theme 14 – TRANSPORT INTO THE STRATOSPHERE**

Report 14: *The contribution of oceanic halocarbons to the stratospheric halogen loading*, Susann Tegtmeyer, Kirstin Krüger, Birgit Quack

## REPORT 1: HALOCARBONS IN THE SOUTH CHINA AND SULU SEA: DISTRIBUTIONS EMISSIONS AND SOURCES

Birgit Quack<sup>1</sup>, Helmke Hepach<sup>1</sup>, Stefan Raimund<sup>1</sup>, Qiang Shi<sup>1</sup>, Wee Cheah<sup>2</sup>, Astrid Bracher<sup>2</sup>

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**Objective:** The oceans have strong influence on the trace gas concentrations in the atmosphere by sea-air-exchange processes. Halogenated hydrocarbons (halocarbons) such as methyl iodide ( $\text{CH}_3\text{I}$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ) and bromoform ( $\text{CHBr}_3$ ) are important trace gases and are biologically and (photo) chemically produced in the water column. Macroalgae along the coast and waters with high phytoplankton densities are known sources for such compounds. River outflow, photochemical reactions and anthropogenic discharges (e.g. treatment of waste water) are other important sources and together with the biological sources cause a highly variable pattern of oceanic halocarbon distribution.

Halocarbons influence the atmospheric chemistry by contributing to the atmospheric halogen pool and consequently influencing the 'oxidizing capacity' of the troposphere and the stratosphere. Whereas naturally produced halocarbons mostly supply to the bromine and iodine pool, anthropogenic halocarbons elevate the atmospheric chlorine pool. In the troposphere, halocarbons influences the  $\text{NO}/\text{NO}_2$  cycle, stimulates catalytic ozone depletion cycles and influences the life times of other trace. Rapid deep convection can transport halocarbons to the lower stratosphere where they may represent significantly to stratospheric halogens and consequently contribute to ozone depletion.

For a better understanding of chemical processes in the atmosphere (especially in a changing atmosphere with elevated greenhouse gases), it is necessary to measure oceanic halocarbon concentrations in so called "hot spots" around the globe. Tropical gas emissions from the ocean towards the atmosphere are highly interesting, because in those areas, trace gases can enter the stratosphere where ascending warm air lifted them upwards. Here, when deep convection events occur, air masses are transported from the troposphere to the lower stratosphere (passing the tropical tropopause layer, which is the typical barrier for ascending air masses in higher latitudes).

### Method

During SO218, the first halocarbon measurements in waters of the coastal western Pacific were performed in the South China and Sulu Sea along the coast off Singapore, Malaysia, Borneo and the Philippines on board the German research vessel *SONNE* during the SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere) campaign.. Halocarbon concentrations were determined in water and air, and sea-to-air fluxes calculated.

Samples were taken along the cruise track at 73 different positions using a submerged water pump under the ship's keel. Moreover, profiles were taken at 10 CTD stations with a 24-bottle CTD rosette (10-L-Niskin bottles). At each station samples were collected in the entire water column with the focus on the upper 150m (surface layer, chlorophyll maximum layer, lower layers).

Halocarbons were analysed on two different purge-and-trap (PT) gaschromatographic systems one with an electron capture detector (ECD) and one with a mass-spectrometric detector (GC-

MS), where the halocarbons were quantified in single ion mode. Quantification of volatiles was performed by external liquid standards. Liquid standards were diluted in seawater and treated like a normal sample. For more details see Quack et al. (2007).

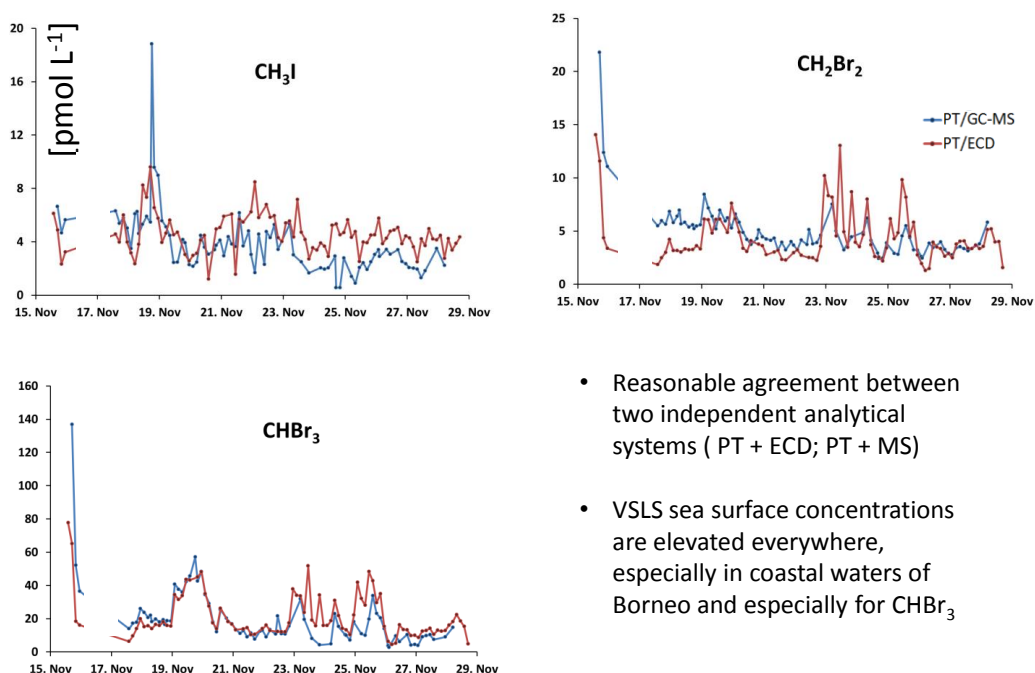


Figure 1: Concentrations of methyl iodide ( $\text{CH}_3\text{I}$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and bromoform ( $\text{CHBr}_3$ ) in surface water, measured with two independent analytical systems.

The halocarbon distribution is highly variable along the cruise track. Near shore samples show typically elevated concentrations, especially for the brominated compounds while samples off shore generally contain lower halocarbons concentrations (Figures 1, 2, 3).

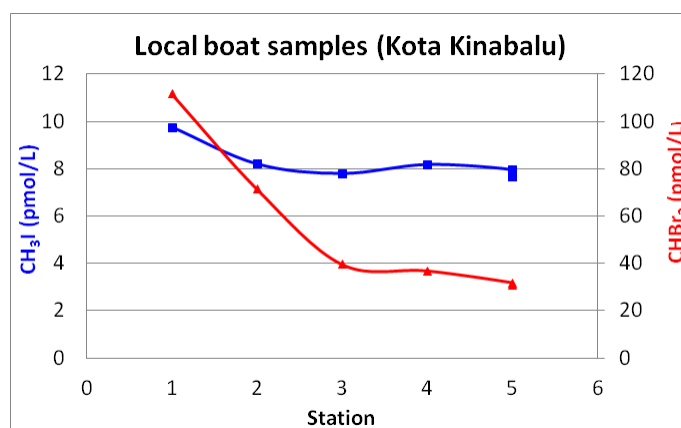


Figure 2: The local boat samples by Kota Kinabalu. Station 1 was closest to the shore, followed in short distance by No, 2 while stations No 3 to 5 where further off shore (see map in Report 13a) .

At Kota Kinabalu, the concentration of bromoform at the local boat station 1 was more than 100 pmol/L, then decreased to 30 pmol/l at station 5. For methyl iodide, the variation of concentration was much smaller.

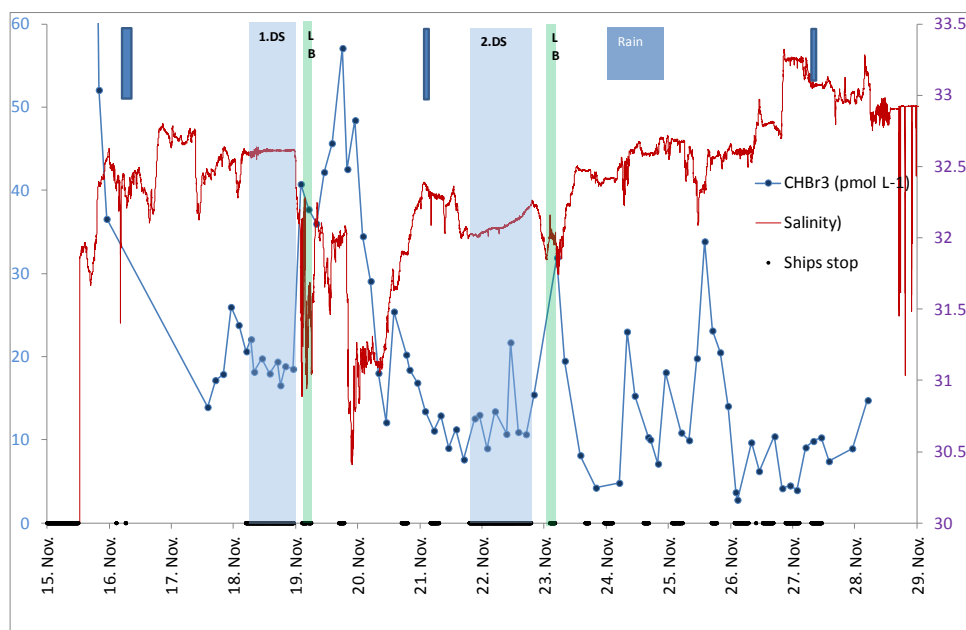


Figure 3: Bromoform and salinity along the cruise track of SO218. Marked are also the diurnal stations (DS), where the ship was positioned on station (ships stop) and the contact with the local boats (LB) at Kuching on the 19<sup>th</sup> and in Kota Kinabalu on the 23<sup>rd</sup> of November 2011. Rain events are also marked.

For bromoform which was the most concentrated halocarbon in sea water, also river run off from the coasts of the Malaysian peninsula and the Borneo coast accounted for a rise in sea water concentrations, which may have several reasons as coastal runoff with natural input (corals?, mangroves?, macro algae?) or anthropogenic sources. Atmospheric  $\text{CHBr}_3$  during the SHIVA-SONNE campaign generally ranged between 2 and 3 ppt in coastal regions and decreased above the more open ocean waters (see also report No 6). The overall regional pattern between oceanic and atmospheric concentration trends was opposite for sea water and atmosphere, while sea water concentrations decreased towards the Sulu Sea, the atmospheric mixing ratios increased, leading to a decreasing concentration gradient between air and sea water in the Sulu Sea compared to the South China Sea (Figure 4).

Form the sea water concentrations and the atmospheric mixing ratios and wind speed, oceanic emissions were calculated, revealing the South China Sea and Sulu Sea as strong source regions of halocarbons for the atmosphere ( Figure 4)

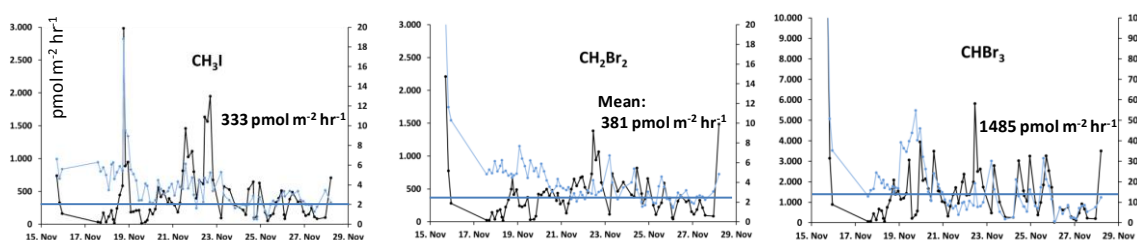


Figure 4: Oceanic emissions ( $\text{pmol m}^{-2} \text{hr}^{-1}$ ) of methyl iodide ( $\text{CH}_3\text{I}$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and bromoform ( $\text{CHBr}_3$ ) from the South China Sea and Sulu Sea (black line), mean emissions and the corresponding saturation anomaly ( $\text{pmol L}^{-1}$ , blue line).

Halocarbon maxima in deeper waters are often coincided with chlorophyll a maxima suggesting a biological source (Figure 5).

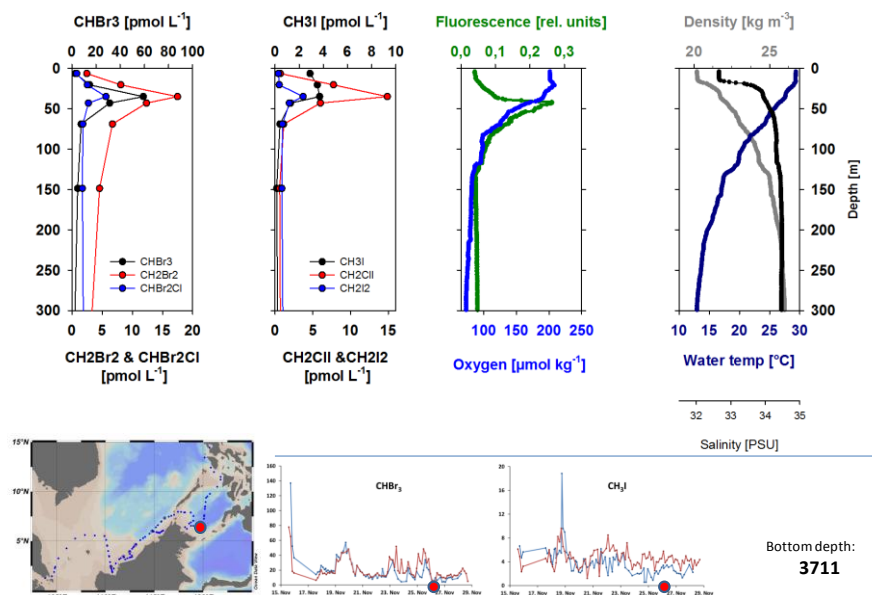


Figure 5: Depth profile of various halocarbons, fluorescence (as measure for chl a), oxygen, water temperature, salinity and density in the Sulu Sea.

The data are available from the GEOMAR data server: <https://portal.geomar.de/> and from the SHIVA ftp server: <ftp://shiva.iup.uni-heidelberg.de> and from Birgit Quack (bquack@geomar.de).

To summarize, the observations show highly variable distributions along the cruise track, hinting to multiple sources and sinks. CTD profiles show elevated concentrations for brominated halocarbons ( $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CHBr}_2\text{Cl}$ ) in the Chl a maximum layer. This strongly indicates a phytoplanktonic source for those compounds. This feature is also visible for the iodinated halocarbons ( $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{BrI}$ ). However, profiles for  $\text{CH}_3\text{I}$  show highest concentration in the subsurface. This indicates a photochemical or biological source at the surface. In some cases, there is a second  $\text{CH}_3\text{I}$  maximum in deeper layers pointing to a second biological source.

Phytoplankton measurements collected during SHIVA-Sonne (SO2018) and analyzed (further details in Report 2a) were used for studying the relationship of phytoplankton to VSLS concentrations in water.

The statistical analysis of the relationship of phytoplankton to different halocarbon species identified significant ( $p < 0.01$ ) relationships between zeaxanthin, cyanobacteria, but also for particulate organic matter (POC and PON) with methyl iodide ( $\text{CH}_3\text{I}$ ) and Kendall's coefficients of 0.45, 0.44, 0.42 and 0.30, respectively. This shows that cyanobacteria likely contribute significantly to the production of  $\text{CH}_3\text{I}$  in the study area, while possible co-correlating factors as sea water temperature and light need to be considered also. Also significant relationships to bromoform ( $\text{CHBr}_3$ ) and dibromomethane were identified for total phytoplankton biomass (TChl-a), hexanoyl-fucoxanthin (the marker pigments for haptophytes) and monovinyl-chlorophyll-b (the marker pigment for prasinophytes). These findings are based on statistical analysis based on Kendall's rank correlation, which examine the ranking relationship between VSLS and phytoplankton groups' marker pigments and total chl a concentration. These results are still written up in a manuscript which is also planned to be submitted to the Special Issue of SHIVA in Biogeosciences (Raimund et al in prep.).



Brominated and iodinated halocarbons also show significant correlations to phytoplankton groups, besides their correlations to the individual pigments (report 2a). Strong correlations were found for the diatoms, haptophytes, prasinophytes and prochlorophytes. The dominant group during the campaign were haptophytes and the prochlorophytes (report 2). Underway data along the cruise track reveal that shallow waters with low salinities show a large influence on near shore halocarbon concentrations.

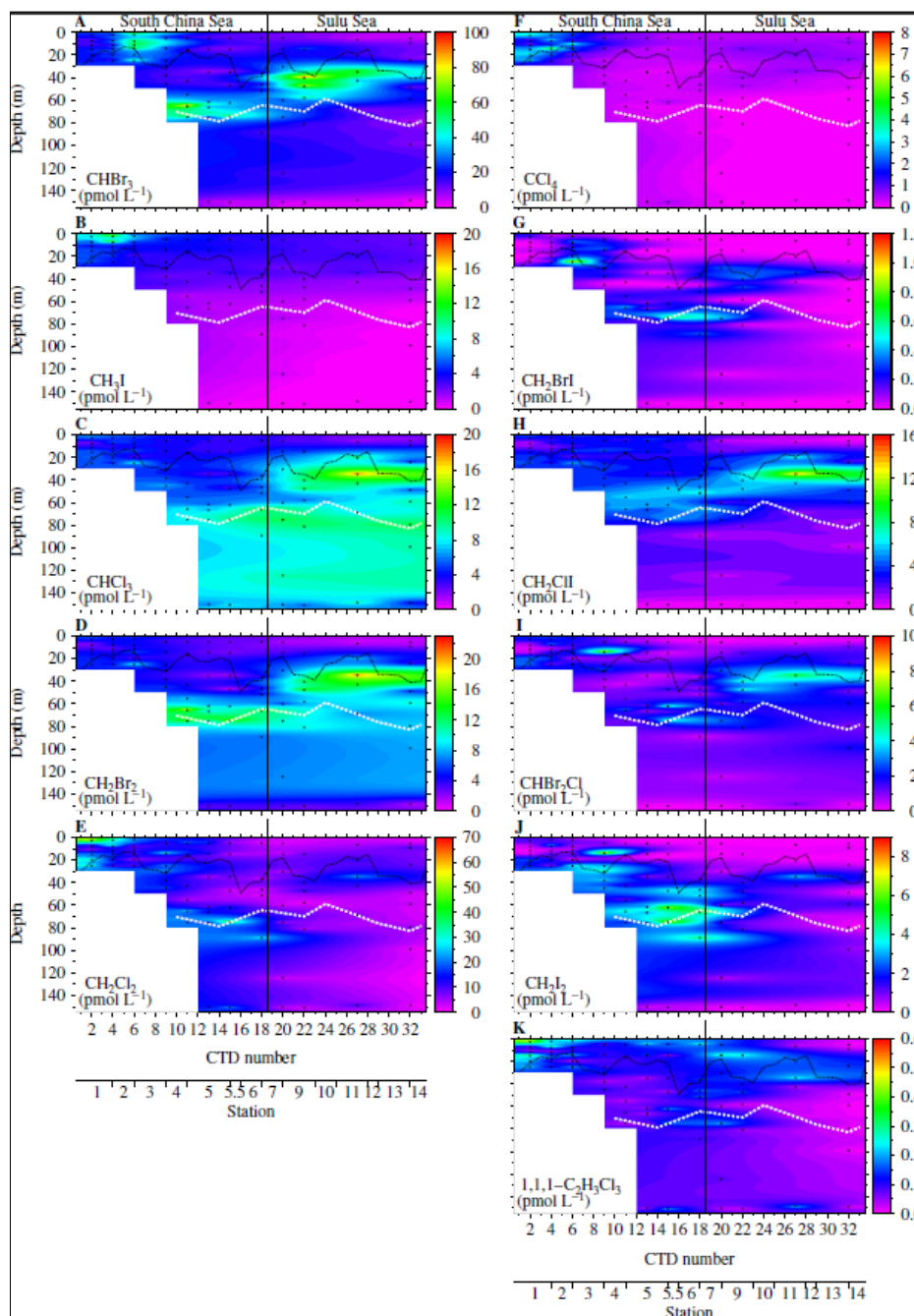


Figure 6: Halocarbon concentrations during SO218 SHIVA-Sonne cruise in the South China and Sulu Sea. Mixed layer (black line) and euphotic (white line) depth (Ref: Wee Cheah, August 2013).

## **REPORT 2A: NATURAL PHYTOPLANKTON COMMUNITIES AND OPTICAL PROPERTIES OF PHYTOPLANKTON DURING SHIVA-SONNE EXPEDITION IN NOVEMBER 2011 IN THE SOUTH CHINA SEA AND SULU SEA, INFINITY ME**

Astrid Bracher<sup>1</sup>, Wee Cheah<sup>1</sup>, Sonja Wiegmann<sup>1</sup>, Mariana Altenburg-Soppa<sup>1</sup>, Joseph Dominic Palermo<sup>2</sup>, Birgit Quack<sup>3</sup>, Stefan Raimund<sup>3</sup>, Gerd Krahmann<sup>3</sup>

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All phytoplankton measurements collected during SHIVASonne (SO2018) and analysed for pigment and group composition, absorption characteristics, physiological conditions were used for studying the relationship of phytoplankton to nutrients and environmental factors (salinity, temperature, wind). First results were presented at the South China Sea Science Conference in Kuala Lumpur (Cheah et al. 2012). Then the phytoplankton parameters such as pigment concentration, functional group type, and PSII efficiency were undergoing a detailed analysis to investigate the relationship between phytoplankton and physical parameters and nutrients. The high horizontal and vertical resolved survey showed that physiological conditions of natural phytoplankton communities in the southern SCS and SS were influenced mainly by light and nutrients concentrations, especially at the surface. Overall, photoacclimation at the shallow coastal stations was affected by high mixing rates and challenged by high surface irradiance. At the deeper offshore stations phytoplankton below the mixed layer were able to maintain higher photochemical efficiency (Fig. 1). Nutrients limitation was the main limiting factor for growth of phytoplankton in these regions as shown by low TChl a concentrations, domination of pico-eukaryotes and cyanobacteria in the open ocean areas. High TChl a concentrations observed at the surface in the shelf areas, especially at stations close to the coast were due to an enhancement in nutrient supplies, probably from river outflows. A manuscript on these results was submitted to Biogeosciences (Cheah et al. BGD 2013).

Satellite monthly mean maps for Nov 2011 for the SHIVASonne cruise area of biomass distributions of different dominant PFTs (Phytoplankton Functional Types; with 30 km by 60 km spatial resolution) derived from measurements of the satellite sensor SCIAMACHY on ENVISAT analyzed with PhytoDOAS, a method of Differential Optical Absorption Spectroscopy (DOAS) specialized for diatoms, dinoflagellates, coccolithophores and cyanobacteria (Bracher et al. 2009, improved by Sadeghi et al. 2012) agree well with the in-situ phytoplankton group data sampled during SHIVASonne (see Fig. 2 for cyanobacteria and coccolithophores). Validation of the HYGEOS-POLYMER MERIS satellite chl-a data showed good correlations ( $r^2$  of 0.77 for 24 collocations) for collocations between in-situ and satellite chl-a, but a general underestimation close to 50% by the satellite product, which is even more pronounced for higher chl-a conc. ( $>0.4 \text{ mg/m}^3$ ). Using the chemtax program the HPLC pigment data were used to calculate the chl-a conc. major phytoplankton groups. These data will supplement other in-situ HPLC phytoplankton data for the validation of the PHYTODOAS retrievals. The outcome of the analysis is expected to result in improved satellite algorithms for deriving phytoplankton characteristics which than can be used for inferring VSLs in water conc. We plan to write up these results together with a more profound analysis of the in-situ optical data in order to improve the satellite products for this region in another paper to be submitted to the SHIVA Special Issue in Ocean Sciences (Bracher et al. in prep.).

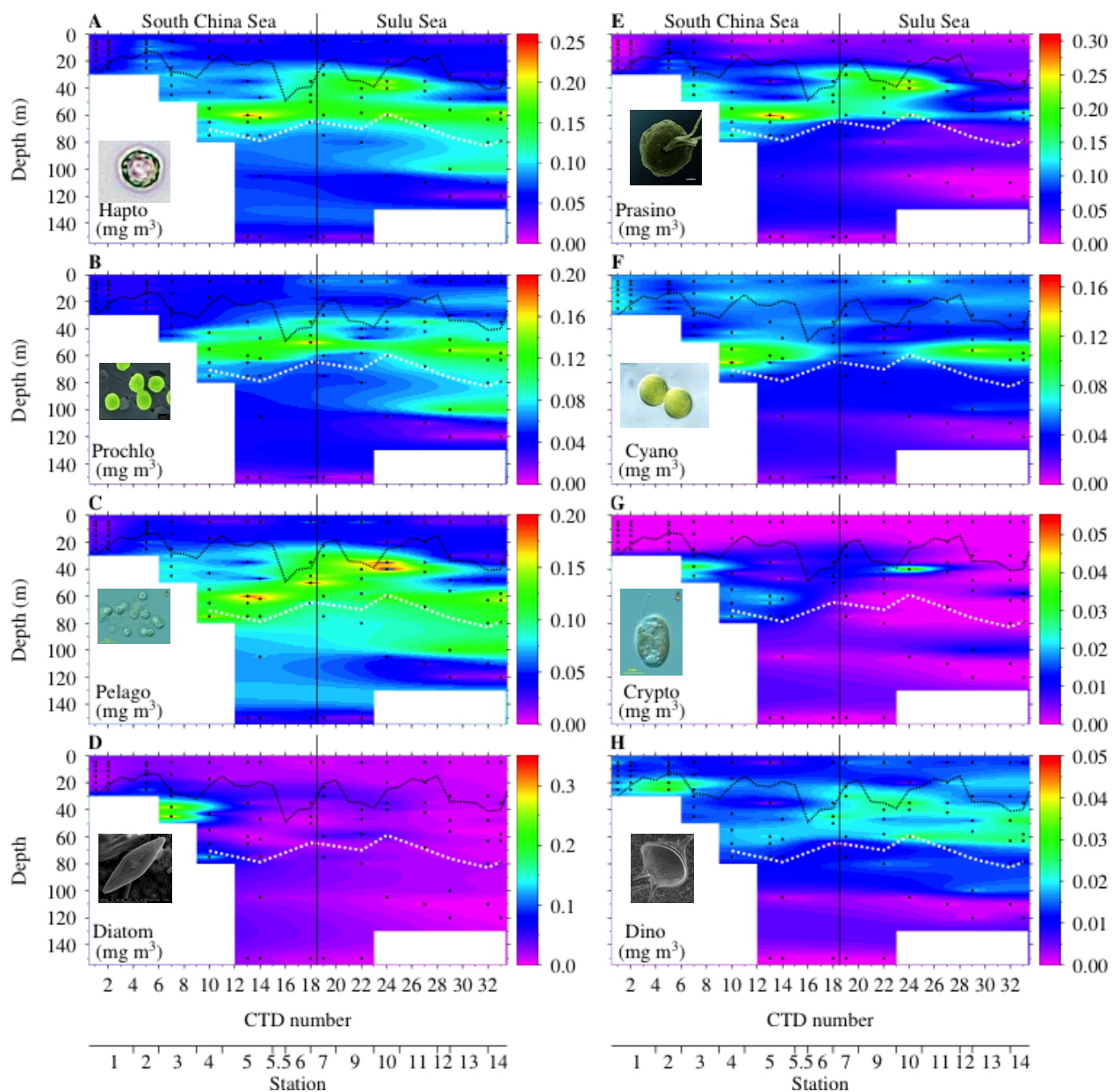


Figure 1: Biomass of different phytoplankton groups during SO218 SHIVA-Sonne cruise as derived from HPLC pigment conc. using the CHEMTAX analysis. In contrast to the surface water, vertical distribution of phytoplankton groups from CTD profiles show phytoplankton communities were dominated by prasinophytes and haptophytes, followed by prochlorophytes and pelagophytes. In general, phytoplankton were observed mostly below the mixed layer and above the euphotic depth correspond to high total chlorophyll a concentration. Figure adapted from Cheah et al. (BGD, 2013)

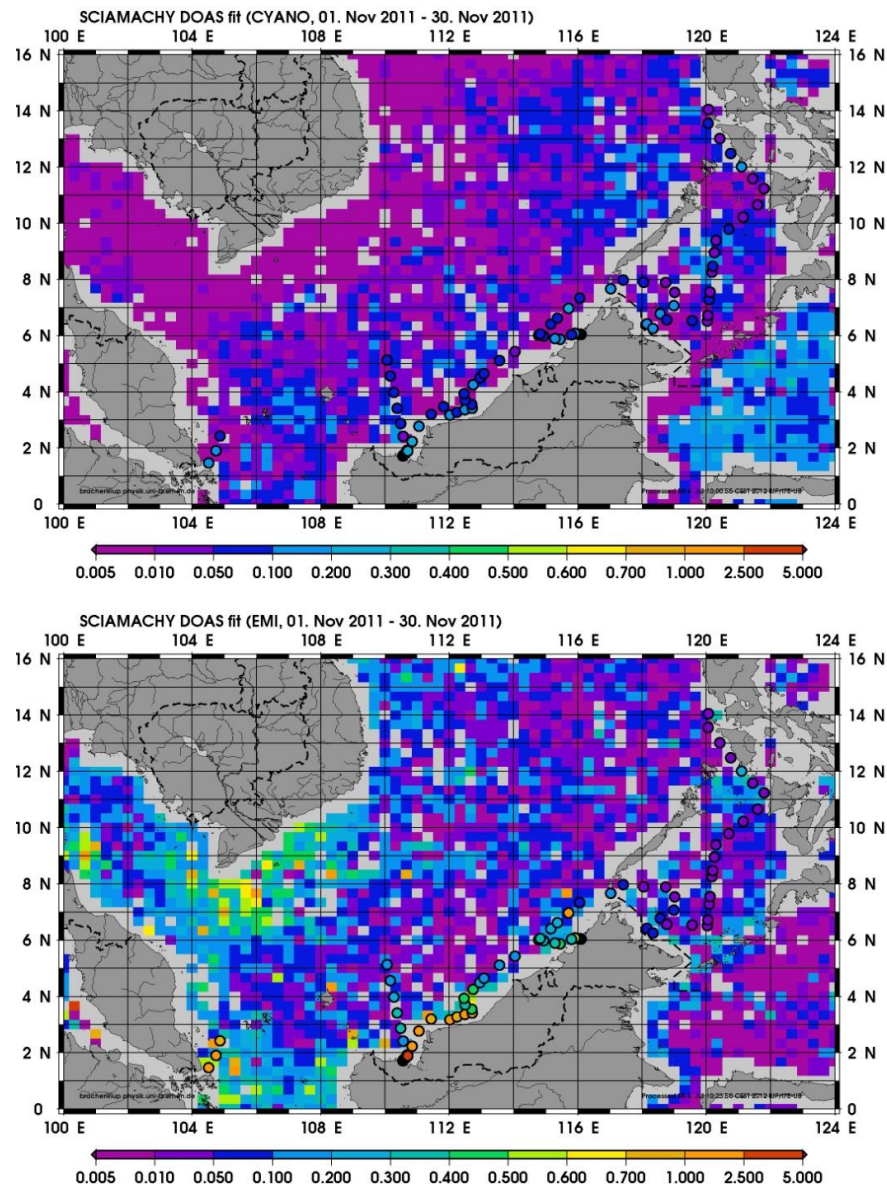


Fig.2: Mean Nov 2011 cyanobacteria (upper level) and coccolithophore (a major group belonging to haptophytes, lower level) chl-a conc. derived from SciAMACHY with PhytoDOAS method. Plotted with the same color scale are the chl-a conc. of cyanobacteria and haptophytes determined via HPLC and CHEMTAX technique at water samples collected in Nov 2011 during the SHIVASonne cruise

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Conference Talk: Cheah W., Taylor B., Dinter T., Raimund S., Quack B., Bracher A. (2012) Community structure and optical properties of phytoplankton during SHIVA-Sonne expedition: From in-situ and satellite. South China Sea Conference 2012, Kuala Lumpur, Malaysia, 22 October 2012 - 26 October 2012

Conference Poster: Hepach H., Raimund S., Taylor B., Bracher A., Fischer T., Quack B. (2013) "Contributions to tropical VLS emissions from the equatorial Atlantic upwelling regions". Poster: SOPRAN Annual Meeting 2013, 19.-20.03.2013, Leipzig, Germany



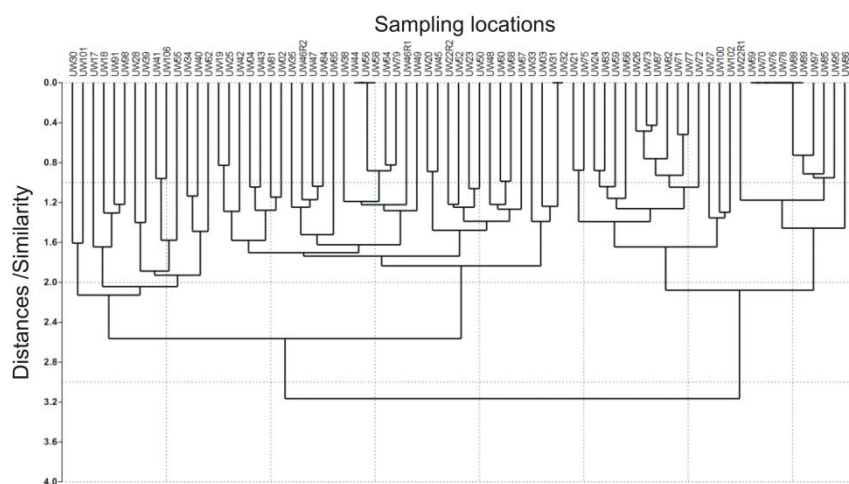
## REPORT 2B: COMMUNITY STRUCTURE OF *PSEUDO-NITZSCHIA* (BACILLARIOPHYCEAE) FROM THE SHIVA EXPEDITION

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A study was undertaken to determine the community structure of *Pseudo-nitzschia* species based on genetic information by using the automated ribosomal intergenic spacer analysis (ARISA). The molecular approach was performed based on the secondary structural information of the first internal transcribed spacer (ITS1) transcripts to characterize the genetic variability of *Pseudo-nitzschia* species along the eastern South China Sea (SCS) during the SHIVA expedition in November 2011. Phytoplankton samples were collected through a 20- $\mu$ m plankton net and retained onto Nylon filter membranes via filtration. Samples were preserved with saline ethanol, and environmental genomic DNAs were obtained in the laboratory. *Pseudo-nitzschia* species- and genus-specific oligonucleotide primers were designed *in silico* based on the secondary structure information. Specificity of the primers was tested on clonal cultures prior to SHIVA samples. Each fragment profile showed the corresponding single fragment and matching ITS1 length *in silico* for each species. Amplification was carried out on a total of 75 surface water samples, and the amplicons were analyzed by fragment analysis using DNA analyzer. Total of 50 ribotypes were detected. Community structure of *Pseudo-nitzschia* along the eastern SCS was characterized. Clustering analysis revealed a degree of community structuring in *Pseudo-nitzschia*. The results showed two linkages, one cluster with locations being dominated by *P. caciantha* ribotype 2; and the other with locations where *P. caciantha* is absent. However, no significant variation was found between samples collected from coastal water or open ocean.

Keywords: *Pseudo-nitzschia*, ribosomal intergenic spacer analysis, species-specific oligonucleotide primers, genotyping



## REPORT 2C: MICROBIAL COMMUNITIES OF THE EASTERN SOUTH CHINA SEA AND THE CELEBES SEA AND THEIR POSSIBLE ROLES IN THE DMS(P) CYCLE

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The South China Sea is a marginal sea that is part of the Pacific Ocean, encompassing an area from the Singapore and Malacca Straits to the Strait of Taiwan (Morton & Blackmore 2001). The Celebes Sea is connected to the South China Sea through the Sulu Sea (Yoshida, Nishimura & Kogure 2007). While the bacterial community structure in these two regions have been previously reported to display some similarities when compared (Yoshida, Nishimura & Kogure 2007) not much is known about the diversity and function of the microbial communities in the South China Sea, especially regarding the eastern region (Kuching and Kota Kinabalu) and the Celebes Sea and no studies on culturable communities in the region have been made at this time. One major and globally important role of surface bacteria is their involvement in the breakdown or osmoregulation of DMSP to DMS or MeSH.

The present study tries to expand our knowledge on microbial communities in the South China Sea by assessing the surface bacterial communities along the eastern region of the South China Sea as well as the Celebes Sea. Over 200 isolates obtained were also screened for the existence of key genes involved in the competing, enzymatically mediated DMSP degradation pathways (*dmdA*, *dddP*) to identify potential key players in the local DMS(P) cycle. This is to our knowledge the first comprehensive study looking at the diversity of culturable bacteria in the eastern South China Sea and also their potential roles in the DMS(P) cycle.

The bacterial communities from the sampling sites in Kuching, Kota Kinabalu and Semporna were found to be diverse with representatives from several groups. The total bacterial assemblage had representatives within the *Alpha*-, *Beta*- and *Gammaproteobacteria*, as well as *Firmicutes* (see Fig. 1). The general similarity in groups (Figure 1) can be explained by the use of a singular isolation media (marine agar at half strength). However, the total number of bacterial isolates obtained and assemblages at the three sampling sites were different as briefly discussed in the following.

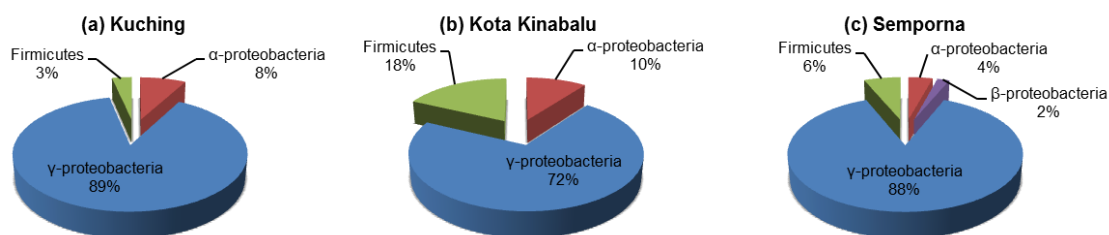


Figure 1: Pie charts illustrating the diversity of bacterial groups based on partial 16S rRNA gene sequences from bacteria isolated from (a) Kuching, (b) Kota Kinabalu and (c) Semporna.

*Gammaproteobacteria* are the dominant phylogenetic group at all three locations and at all sampling depths, followed by *Alphaproteobacteria* (see Fig. 1). *Betaproteobacteria* were only found at Semporna at 1m depth. From Kuching waters, 89 isolates were obtained over two sampling periods (November 16 and 19, 2011). The diversity of bacterial phylotypes is presented in Figures 2 to 5. Overall, 89% of the cultured bacteria were clustered within the *Gammaproteobacteria*, 8% within the *Alphaproteobacteria* and 3% within the *Firmicutes* (Figs. 2+3). In Kota Kinabalu waters, 39 isolates were obtained and the majority (72% of the cultured bacteria) were clustered within the *Gammaproteobacteria*. The remaining isolates were members of the *Firmicutes* (18%) and *Alphaproteobacteria* (10%) (Fig. 4). In Semporna waters, 48 isolates were obtained from four phylogenetic groups. In total, 88% of the cultured bacteria were members of the

*Gammaproteobacteria*, 6% of the *Firmicutes*, 4% of the *Alphaproteobacteria* and 2% *Betaproteobacteria* (Fig. 5).

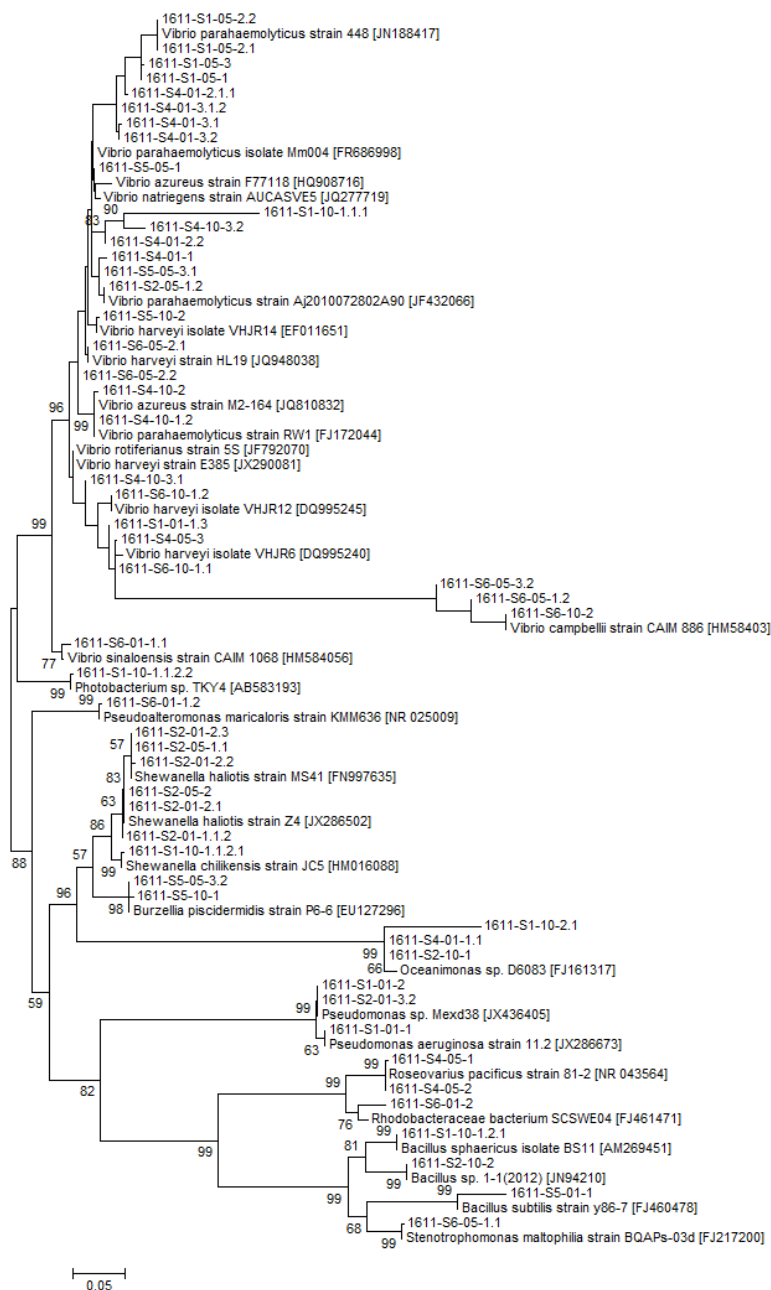


Figure 2: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Kuching 1611. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbour-joining method. Bootstrap values  $\geq 50$  are shown and the scale bar represents a difference of 0.05 substitution per site. Accession numbers for the reference sequences are indicated.



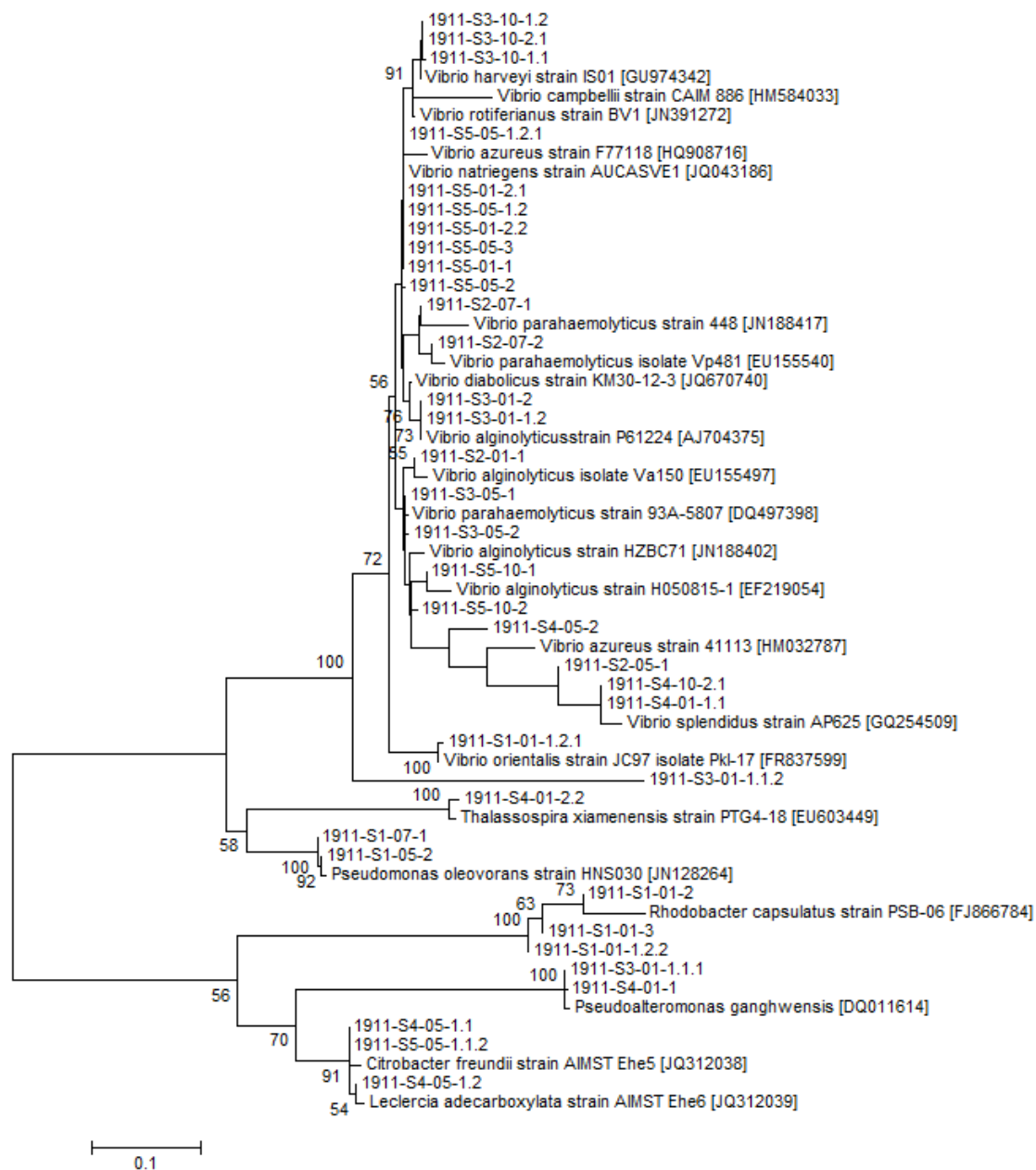


Figure 3: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Kuching 1911. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbor-joining method. Bootstrap values  $\geq 50$  are shown and the scale bar represents a difference of 0.1 substitution per site. Accession numbers for the reference sequences are indicated.

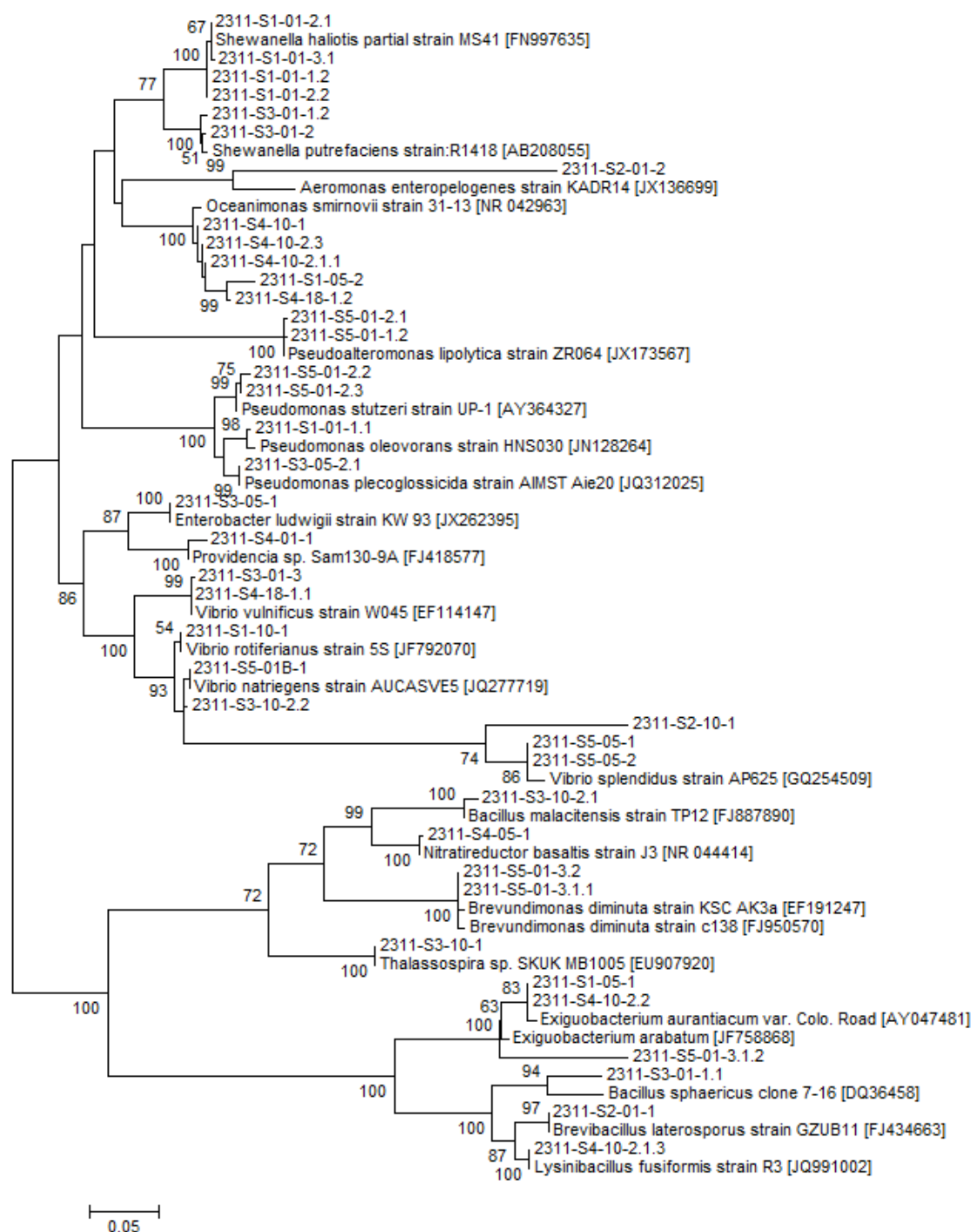


Figure 4: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Kota Kinabalu. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbor-joining method. Bootstrap values  $\geq 50$  are shown and the scale bar represents a difference of 0.05 substitution per site. Accession numbers for the reference sequences are indicated.

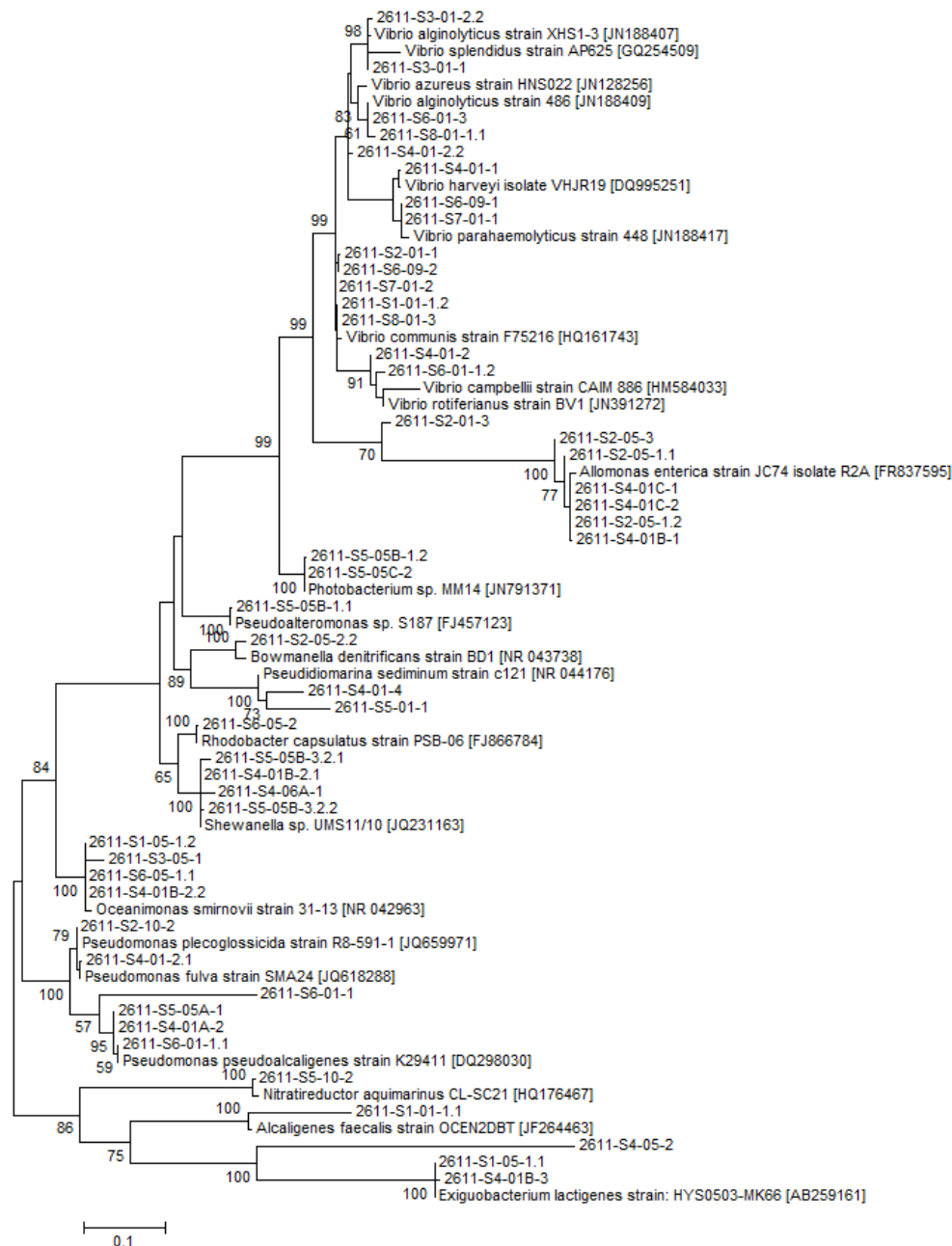


Figure 5: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Semporna. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbour-joining method. Bootstrap values  $\geq 50$  are shown and the scale bar represents a difference of 0.1 substitution per site. Accession numbers for the reference sequences are indicated.

Our results correlate with existing records of microbial communities found in coastal and open-ocean environments (Bernard et al. 2000) although samples from Kuching display significant riverine influence. Differences between the three areas can partly be explained by differences in physico-chemical parameters. The Kuching community is influenced by higher nutrients and riverine input, and is dominated by potentially pathogenic *Vibrios*, while the Kota Kinabalu community is more indicative of an open ocean environment. Isolates obtained from Kota Kinabalu and Semporna show that the communities in these areas have potential roles in bioremediation, nitrogen fixing and sulphate reduction.

Since there are no published reports on the microbial biodiversity in the eastern region of the South China Sea, their role in local biogeochemical cycles is also unclear. To date, there are no available reports on the sulphur cycle in the region, or of DMSP catabolism from bacterial communities of Kuching, Kota Kinabalu and Semporna; neither are any bioinformatics data available on the prevalence of *dmdA* and *dddP* genes in bacteria from these regions. As part of our effort to understand the importance of bacteria in the region for the local sulphur cycle, we screened our isolates for the existence of *dmdA* and *dddP* genes. Since our isolates have been cultured in a very general way using a method that does not involve selection for DMSP utilisation, any presence of these genes in our isolates is most likely a fundamental trait of these bacteria.

Bacteria isolated from Kuching displayed the highest abundance of both DMSP degrading genes (36%) compared to communities isolated from Kota Kinabalu and Semporna with 13 and 19 %, respectively. The bacterial community in Kota Kinabalu has the highest percentage of *dmdA* gene occurrence (28%) while the *dddP* gene responsible for DMS production appears to be most abundant (29%) within the bacterial community Semporna (see Fig. 6)

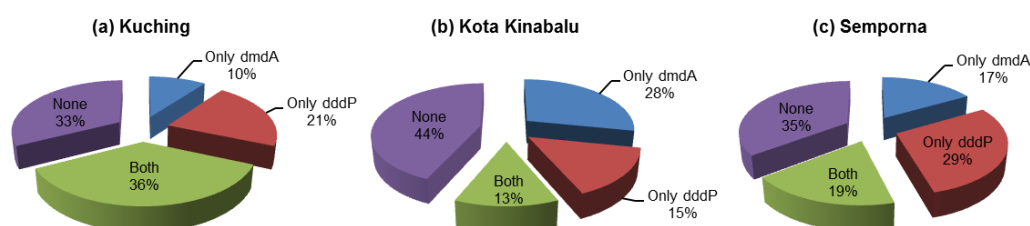


Figure 6: Relative abundance of *dmdA* and *dddP* genes in cultured bacterial communities from the waters of (a) Kuching, (b) Kota Kinabalu and (c) Semporna.

The *Gammaproteobacteria* group is the largest identified fraction within the communities at all three sampling sites with the potential for DMSP-assimilation. Interestingly, the composition of the DMSP-assimilating community generally mirrored the composition of the total bacterial community at each sampling site which is unlike previous studies at the Gulf of Maine and the Sargasso sea where the dominating group are the *Alphaproteobacteria* (Malmstrom, Kiene & Kirchman 2004). Our findings indicate that the community structure of *Gammaproteobacteria* in the area could be tightly linked to the local sulphur and also possibly the nitrogen cycle.

It was previously hypothesized that DMSP production is an overflow mechanism for when growth is unbalanced by lack of nutrients and the need to release excess energy and excess reduced sulphur (Stefels 2000). These carbon-energy overflow substances might evolve through natural selection to be useful in the cell (e.g. through auxiliary structures or defence mechanisms) (Hill, White & Cottrell 1998). Based on our findings, it seems likely that at low nutrient conditions, the distribution of *dmdA* and *dddP* genes within the bacterial community become more specific (e.g. more *dmdA* in KK and more *dddP* in Semporna; see Figure 3.11) to adapt to a preferred pathway to degrade DMSP.

Further in-depth characterization of these communities through a combination of physical, chemical and molecular biological studies will improve our understanding of the role of bacteria in DMS(P) cycling in the eastern South China Sea and the Celebes Sea and their impacts on climate change.

## REPORT 2D: CULTURABLE BACTERIA FROM TALANG-TALANG REEF AND ITS SURROUNDING WATERS

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Coral reefs are a rare feature in Sarawak due to its shallow sea shelf extending a long way into the ocean. The reefs of Sarawak are limited to the areas off the shores of Bintulu, Miri and offshore islands including the Talang-Satang region in Kuching. The Talang-Satang region is situated off the coast of Sematan and is especially important as it is one of the most diverse ecosystems found off Sarawak, including a healthy coral reef.

The coral surface mucus layer (SML) contains a complex microbial community that respond to changes in the environment (Ritchie & Smith 2004). The normal microbial flora within the SML can protect the coral against pathogen invasion and disturbances which may have led to coral diseases (Sutherland, Porter & Torres 2004). On average, 20-30 % of bacterial isolates originating from coral SML possess antibacterial properties (Ritchie 2006) that may assist the coral holobiont as a first line of defence against pathogens (Shnit-Orland & Kushmaro 2009). It has been suggested that these antimicrobial compounds are temperature sensitive (Ritchie 2006). Antibacterial activity was found to be optimal at 26 °C and slightly decreased at 30 °C, with partial inactivation occurring at 60 °C and complete loss of activity occurring at 80 °C (Shnit-Orland & Kushmaro 2009).

Coral reefs are also potentially significant sources of dissolved DMS and DMSP, particularly when corals are stressed or exposed during low tides (Broadbent & Jones 2004). The concentrations of DMS and DMSP measured in mucus are the highest reported in the marine environment, with values exceeding those reported from highly productive polar waters (Fogelqvist 1991; Trevena et al. 2000, 2003) and sea algal communities (Kirst et al. 1991; Levasseur, Gosselin & Michaud 1994; Trevena et al. 2003). The high levels of DMSP and DMS produced by corals, coupled with involvement of bacteria in DMSP and DMS conversion, suggest that corals are likely to harbor bacterial species involved in the cycling of these compounds (Raina et al. 2009, 2010).

The present study provides what we believe is the first analysis of cultured bacterial communities from the reefs of Talang- Talang. The bacterial communities from coral mucus, reef sediment and water column were found to be diverse with representatives from several bacterial groups. The total bacterial assemblage had representatives within the *Actinobacteria*, *Proteobacteria* (*Alpha*- and *Gammaproteobacteria*), as well as *Firmicutes* (see Fig. 1 for an overview of the major groups). The total number of bacterial isolates obtained and assemblages from the three reef environments are discussed in the following.

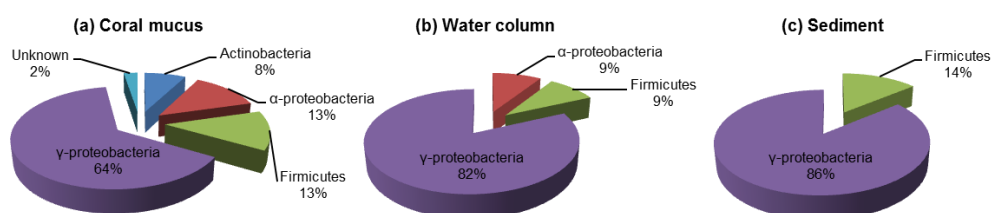


Figure 1: Pie charts illustrating the diversity of bacterial groups based on partial 16S rRNA gene sequences from bacteria isolated from (a) coral mucus, (b) water column and (c) sediment.

A total of 93 isolates were cultured from coral mucus, water column and reef sediment of the Talang-talang reef. Overall, 3% of the cultured bacteria were clustered within the *Actinobacteria*, 76% within the *Gammaproteobacteria*, 6% within the *Alphaproteobacteria* and 13% within the *Firmicutes*. From the coral mucus, 39 isolates were obtained with the majority clustered within the *Gammaproteobacteria* (64%), followed by *Alphaproteobacteria* (13%), *Firmicutes* (13%) and *Actinobacteria* (8%). There is an unknown isolate that was cultured from coral mucus. Its closest related sequence is unidentified. Within the water column, 82% of the isolates were *Gammaproteobacteria*, 9% *Actinobacteria* and 9% *Firmicutes*. Isolates from reef sediment were less diverse with cultures from only two bacterial groups: the *Gammaproteobacteria* (86%) and *Firmicutes* (14%).

The mucus associated isolates are related to representatives of bacteria documented in earlier studies, including a subset of *Vibrio* spp. consistently found in association with healthy corals (Ritchie & Smith 1995a, 1995b, 2004). There is a higher percentage of *Vibrios* (91%) when comparing mucus attached isolates to mucus associated isolates (29%). This illustrates the defensive qualities of coral mucus, and how a potential composition shift from beneficial bacteria to *Vibrio* dominance (which are known to be opportunistic) under conditions of increased temperature can occur.

Isolates related to the *Alphaproteobacteria* are only found in coral mucus samples. A couple of the cultures are related to uncultured sequences suggesting possible novel species. Isolates related to *Roseobacter* spp. and *Sphingobium amiense* strain D3AT58 (GenBank accession number JF459959; 97% similarity) were also obtained. *Roseobacter* spp. are widely associated with corals (Frias-Lopez et al. 2002; Rohwer et al. 2002; Bourne & Munn 2005; Kooperman et al. 2007; Bourne et al. 2008) and are potentially central to the health of corals. Antibacterial activities of *Roseobacter* have been observed against a wide range of marine pathogens (Hjelm et al. 2004). Coral associated bacteria from this genus have also been previously implicated in the degradation of DMSP (Raina et al. 2009, 2010). Thiotropocin, an antibiotic produced by *Roseobacter*, is a sulfur compound that might be derived from DMSP metabolism (Wagner-Döbler et al. 2004). These bacteria are suspected to be involved in a symbiotic relationship with coral-cultured zooxanthellae (Raina et al. 2009) which produces high concentrations of DMSP (Hill, Dacey & Krupp 1995; Broadbent, Jones & Jones 2002; Van Alstyne, Schupp & Slattery 2006). It is likely that the occurrence of *Roseobacter* spp. within the coral mucus may be due to the availability of DMSP produced by the zooxanthellae. *Roseobacter*-related strains (BCM 37 and 56; 100% similarity) were isolated from the coral mucus. Both isolates may play a possible role in the biogeochemical cycling of sulphur within the mucus as they appear to have both DMSP degrading genes. The *Roseobacter* genus is potentially central to the health of corals. The *Roseobacter* spp. are widely associated with corals (Frias-Lopez et al. 2002; Rohwer et al. 2002; Bourne & Munn 2005; Kooperman et al. 2007; Bourne et al. 2008) and suspected to be involved in a symbiotic relationship with zooxanthellae (Raina et al. 2009). An antibiotic produced by *Roseobacter*, thiotropocin, is a sulphur compound derived from DMSP metabolism (Wagner-Döbler et al. 2004).

To our knowledge, screening of *dmdA* and *dddP* genes in coral SML bacterial communities has not been done before. This preliminary study is part of our effort to understand the importance of bacteria in the region for the local sulphur cycle. Our isolates were not cultured in a method that involves specific selection for DMSP utilisation, therefore any presence of these genes in our isolates is most likely a fundamental trait.

The *dddP* gene which is responsible for DMS production appears to be most abundant (26%) within the coral mucus bacterial community (see Fig. 2). Many of our isolates also show potential in undergoing both DMSP degrading pathways as 20% of them have both *dmdA* and *dddP* genes.

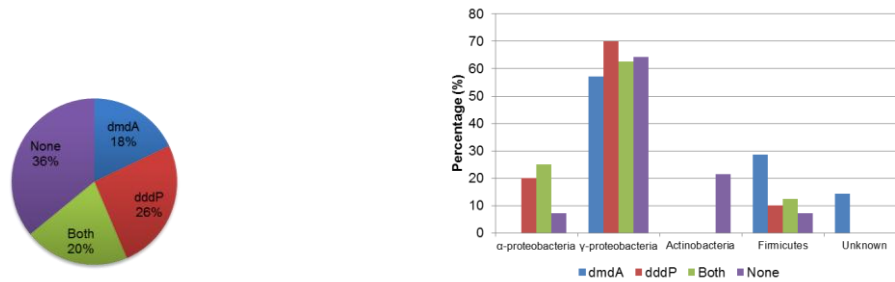


Figure 2: a) Relative abundance of dmdA and dddP genes in cultured bacterial communities from coral mucus. b) Presence of dmdA and/or dddP genes in bacterial isolates from coral mucus.

The presence of DMSP degrading genes in the coral mucus bacterial groups is similar to their occurrence in bacterial communities in the Kuching area of the South China Sea (see report on Bacterial diversity in SCS) where their composition generally mirrored the bacterial community. The *Gammaproteobacteria* group is the largest identified fraction within the community with the potential for DMSP-assimilation, followed by the *Alphaproteobacteria* and *Firmicutes*.

Within the coral mucus, bacteria are extremely dependent on photosynthetic products produced by zooxanthellae which play a role in regulating microbial communities present in corals (Ritchie & Smith 2004). Studies into coral-associated bacteria capable of metabolizing DMSP and DMS have emerged only recently (Raina et al. 2009, 2010). Little information is available and the nature of their interactions with the coral host remains an important research question.



### REPORT 3: INTERACTION OF CLIMATE ACTIVE GASES DURING THE SHIVA-SONNE SO218 CAMPAIGN: DIMETHYLSULFIDE, OXYGENATED VOLATILE ORGANIC COMPOUNDS, NITROUS OXIDE (N<sub>2</sub>O), AND METHANE (CH<sub>4</sub>)

Christa Marandino, Cathleen Zindler, Hermann W. Bange (not on board), and Franziska Ziska (on board for H. Bange)

Helmholtz-Center for Ocean Research Kiel GEOMAR, Marine Biogeochemistry, Chemical Oceanography, Kiel, Germany

**Objective:** To investigate seawater cycling and the air-sea gradient of a variety of climate-active trace gases. Specifically, nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>), dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP), dimethylsulfoxide (DMSO), isoprene, and 11 different oxygenated volatile organic compounds (OVOCs): methanol, ethanol, n-propanol, isopropanol, 1-butanol, 2-butanol, acetaldehyde, propanal, butanal, acetone, and butanone were measured. The relationship between the concentrations of these compounds with each other and a variety of biological, chemical and physical parameters will be examined in order to determine what factors control the magnitude and distribution of the compounds in the surface ocean.

#### Background

##### *Nitrous oxide and methane*

Nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) are atmospheric trace gases, which, directly and indirectly, influence the present-day climate of the Earth. Thus, an assessment of the natural and anthropogenic sources and sinks as well as the formation pathways of N<sub>2</sub>O and CH<sub>4</sub> is essential both to understand past Earth's climate variability and to estimate the future development of Earth's climate. The world's oceans including its coastal zones, as natural sources of N<sub>2</sub>O and CH<sub>4</sub>, play a major role in the global budget of atmospheric N<sub>2</sub>O, but only a minor role in the global budget of atmospheric CH<sub>4</sub>. However, measurements of oceanic N<sub>2</sub>O and CH<sub>4</sub> are still sparse and the derived emission estimates are associated with large uncertainties. N<sub>2</sub>O in oceanic environments is mainly formed as a byproduct during nitrification (NH<sub>4</sub><sup>+</sup> → NH<sub>2</sub>OH → NO<sub>2</sub><sup>-</sup> → NO<sub>3</sub><sup>-</sup>) and as an intermediate during denitrification (NO<sub>3</sub><sup>-</sup> → NO<sub>2</sub><sup>-</sup> → N<sub>2</sub>O → N<sub>2</sub>). In both processes, the yield of N<sub>2</sub>O strongly depends on the concentration of dissolved oxygen (O<sub>2</sub>). Both, nitrification and denitrification are microbial processes and can occur in the water column, in the sediments and in the interior of suspended particles.

CH<sub>4</sub> is formed during the decomposition of organic material by microbial methanogenesis. Since CH<sub>4</sub> formation requires strictly anaerobic conditions, CH<sub>4</sub> is produced in anoxic environments such as sediments, in the interior of suspended particles, in zooplankton guts during grazing or from biological cleavage of dissolved precursors such as DMSP and methylphosphonate. Additionally, CH<sub>4</sub> is oxidized under aerobic as well as anaerobic conditions in the water column and in the sediments. On the continental shelf so-called geological CH<sub>4</sub> can be released directly to the water column through mud volcanoes, via groundwater input, or seepage from gas/oil fields.

##### *DMS(P/O)*

DMS is the most abundant biogenic sulfur compound emitted to the atmosphere. It is mainly produced in the surface ocean from the precursor DMSP, a compound excreted by phytoplankton. Once in the atmosphere, DMS is rapidly oxidized to sulfur dioxide (lifetime approximately 1 day). The oxidation products of DMS can form aerosols and cloud condensation nuclei, thereby influencing the Earth's radiative properties and climate. It was proposed by Charlson et al. (1987) that this air-sea cycling of DMS may be a natural negative feedback loop on Earth's climate system. This so called CLAW hypothesis has yet to be proven. In addition, it is still not possible to predict the concentrations and distribution of DMS in the surface ocean. Although many individual components of surface ocean DMS cycling have been studied, such as production of DMSP by dinoflagellates and cleavage of DMSP into DMS via DMSP lyase, the surface ocean concentrations of DMS seem to be due to a combination of factors. One part of the cycle, DMS oxidation, produces the product, DMSO. DMSO is

found throughout the water column, even into the deep ocean. More studies investigating exactly what factors (e.g. phytoplankton species, bacteria abundance, UV radiation, etc.) control the surface ocean cycling and concentrations of DMS are still needed.

### *OVOCs*

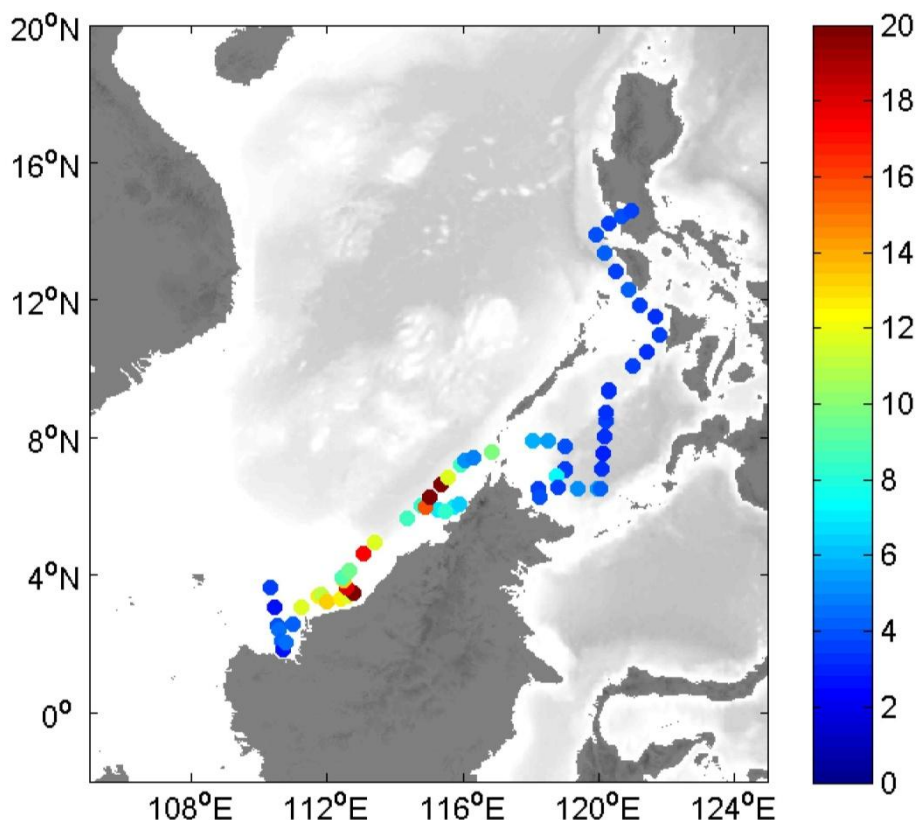
OVOCs can influence the oxidative capacity of the atmosphere by contributing to peroxyacetylnitrate and secondary organic aerosol formation, and  $\text{HO}_x$  and ozone chemistry. They are especially important in regions of the atmosphere where water vapor levels are low, such as in the upper troposphere. The region of the Shiva Sonne cruise track is especially interesting because of the highly convective air in this region. Gases produced at the air-sea interface can be transported more quickly and directly to the upper troposphere/lower stratosphere, where they have the greatest impact on atmospheric chemistry. Whether the ocean is a source or a sink of these compounds to the atmosphere is still an open question. In addition, surface ocean processes of OVOCs are largely uncharacterized, but it is largely thought that OVOCs are produced by photochemical reactions of color dissolved organic matter (CDOM) and by biology in the surface ocean. Uptake of these compounds also seems to be related largely to biological processes.

### **Methods**

Samples for the determination of dissolved  $\text{N}_2\text{O}$  and  $\text{CH}_4$  have been taken in triplicates from both the continuous surface seawater supply and the CTD/rosette casts. Samples have been poisoned with  $\text{HgCl}_{2(\text{aq})}$  immediately after sampling. All samples were shipped back to our lab in Kiel for the analysis of dissolved  $\text{N}_2\text{O}$  and  $\text{CH}_4$ .  $\text{N}_2\text{O}$  and  $\text{CH}_4$  will be determined by applying the static headspace equilibration method. Gaseous subsamples of the equilibrated headspace will be injected onto a separation column filled with 5A molsieve followed by detection of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  with an electron capture detector (ECD) and a flame ionization detector (FID), respectively. 106 underway samples have been sampled for  $\text{N}_2\text{O}$  and  $\text{CH}_4$  in triplicates every 3h from the continuous surface seawater supply. 14 CTD/rosette casts and 7 CTD/rosette casts have been sampled for  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , respectively. The final  $\text{N}_2\text{O}$  and  $\text{CH}_4$  data will be archived in MEMENTO (The MethanE and NiTrous Oxide database: <https://memento.ifm-geomar.de/>).

DMS, DMSP (dissolved and particulate), and DMSO are measured by purge and trap gas-chromatography (GC) coupled to a flame photometric detector (FPD). Triplicate samples, 10 mL in volume, are sparged for 10 minutes with a helium flow of approximately 30 mL per minute. The samples are dried with potassium carbonate and trapped with liquid nitrogen before being injected on the GC with boiling water. DMSP and DMSO are quantitatively converted to DMS via 26 chemical reaction after the sample has been sparged of the ambient DMS. The subsequent concentrations of DMS are measured in the way described above.

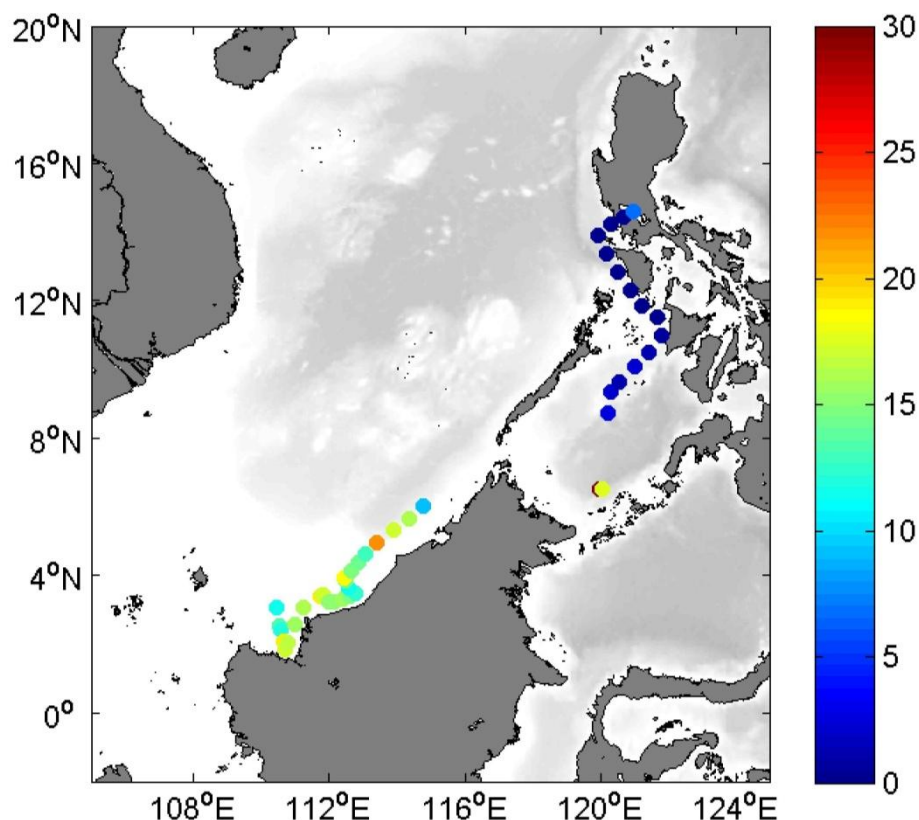
OVOCs, isoprene, and DMS were also measured via purge and trap gas chromatography coupled to a mass spectrometer detector (GC-MS). 10 mL samples were sparged with 30 mL per 27 minute of helium for 20 minutes through a potassium carbonate drying trap. The trap was then flushed at 40 mL per minute for an additional 10 mins. The sparged gases were trapped with liquid nitrogen then injected onto the GC column with boiling water. The masses of each compound were detected with the MS. Trace gases in air were trapped for 10 minutes in liquid nitrogen headspace from the bow of the ship using a small pump (flow = approx. 80 mL per minute). Potassium carbonate was again used to dry the samples. The gases were desorbed with boiling water and refocused using liquid nitrogen before being injected on the GC and detected in the same way as the liquid samples. Standards for both air and water were measured daily and 3 4 to 5 point calibrations for air and water were performed over the entire cruise track. CDOM fluorescence was measured to characterize the chemical makeup of the CDOM. CDOM absorbance was measured to determine the quantity in the seawater samples.



**Figure 1. Surface seawater  $\text{CH}_4$  levels (nM) over the SHIVA-Sonne cruise track.**

#### **DMS(P) as a source of $\text{CH}_4$**

Methane is oversaturated in the subsurface layer of ocean relative to the atmosphere (Figure 1). Methanogenesis, the only known source of methane, is strictly anaerobic. Therefore, since these conditions do not exist in the upper ocean, another source of methane should exist. Some hypotheses suggest that methane is formed in anoxic niches or in the intestines of fish. Recent investigations propose two alternative  $\text{CH}_4$  production mechanisms, both implicating nutrient limitation in the control of mixed layer  $\text{CH}_4$  formation. In the first hypothesis bacterioplankton successfully exploit phosphate-depleted waters, where nitrate ( $\text{NO}_3^-$ ) is in excess, by deriving phosphorus from phosphonates such as methyl phosphonate (Karl et al. 2008). Methane is thus produced aerobically as a byproduct of methyl phosphonate decomposition. The second hypothesis proposes that certain microbes can catabolise DMSP as a carbon source through methylotrophic methanogenesis in  $\text{NO}_3^-$  depleted waters, where phosphate ( $\text{PO}_4^{3-}$ ) is plentiful (Damm et al. 2010). Based on the conversion of DMSP to hydrogen sulphide ( $\text{H}_2\text{S}$ ) and  $\text{CH}_3\text{SH}$  by DMSP-utilising bacteria (Kiene et al. 2000) and a recent proposal for the intermediate formation of  $\text{CH}_3\text{SH}$  during  $\text{CH}_4$  oxidation (Moran et al. 2008), Damm et al. (2010) proposed a thermodynamically plausible reverse reaction for the aerobic production of  $\text{CH}_4$  from  $\text{CH}_3\text{SH}$ . The two mechanisms are entirely compatible and raise the intriguing possibility that deviations from the Redfield N:P ratio could be indirectly responsible for the marine  $\text{CH}_4$  paradox through planktonic succession favouring species able to exploit alternative marine phosphorus and nitrogen stores. On the SHIVA-Sonne cruise, it is clear that there are similarities in the spatial distribution of the DMS and methane, possibly indicating DMSP as the main source for both (Figure 1 and 2).



**Figure 2. Surface seawater DMS concentrations (nM) over the SHIVA-Sonne cruise track.**

#### **Further preliminary results and data analysis plan**

Unfortunately, the GC-FPD system did not exhibit adequate sensitivity during the cruise. Most samples were measured with the gas chromatograph-mass spectrometer system. Separate samples were preserved for DMS, DMSP, and DMSO detection later. The DMS values measured in situ do not compare well with those preserved (Table 1). The explanation for this discrepancy is not currently apparent and tests to understand the analytical differences are on-going. DMS concentrations were between 0 and 25 nM (Figure 2). There are clear hot spots along the Borneo coast in the South China Sea, while the levels drop markedly in the Sulu Sea off the Philippines coast. Analyses of phytoplankton pigment distribution for comparison with the DMS surface seawater data are currently underway. Methanol, acetone, isopropanol, DMS and 1-butanol were observed in almost every sample. Acetaldehyde, ethanol, propanol, and 2-butanol were also regularly measured. Propanal, isoprene, butanal, and butanone were either extremely small (below the detection limit) or not present in most of the samples measured.

More detailed analysis is planned for DMS(P/O), OVOCs, and  $N_2O$ . The air-sea gradient and spatial distribution over the cruise track is yet to be determined. CTD profiles for DMS and the CTD chlorophyll maximum depth for OVOCs and isoprene were also measured but the results will be analyzed in Fall 2013. CDOM absorbance values cannot be determined because the spectrophotometer lamp was not functioning properly. CDOM fluorescence data has been examined for quality control and data will be finalized in Fall 2013.

**Table 1. Comparison of GC-MS DMS measurements made on board to GC-FPD measurements preserved and measured at IFM-GEOMAR. ND indicates samples values below the detection limit.**

Day of Year	DMS (mol L <sup>-1</sup> , GC-FPD)	DMS (mol L <sup>-1</sup> , GC-MS)
322.05	ND	1.033E-08
322.17	ND	1.247E-08
322.30	ND	8.557E-09
322.80	ND	8.350E-09
322.92	ND	6.732E-09
323.05	ND	1.130E-08
323.17	ND	8.874E-09
323.29	ND	8.523E-09
323.42	ND	7.375E-09
323.55	ND	7.916E-09
323.67	ND	1.108E-08
323.79	ND	8.965E-09
323.92	ND	6.729E-09
324.04	ND	6.851E-09
324.17	ND	7.572E-09
324.29	ND	6.305E-09
324.42	ND	3.608E-09
324.55	ND	2.582E-09
324.67	ND	5.842E-09
324.80	ND	1.087E-08
324.92	ND	6.164E-09
325.05	ND	5.613E-09
325.17	ND	6.102E-09
325.29	ND	4.379E-09
325.42	ND	1.430E-08
325.55	ND	9.022E-09
325.67	ND	8.072E-09
325.80	ND	5.764E-09
325.92	ND	1.411E-10
326.04	ND	5.176E-09
326.30	5.530E-08	5.422E-09
326.42	ND	4.049E-09
326.54	ND	4.732E-09
326.68	ND	4.102E-09
326.92	ND	3.599E-09
327.04	ND	1.464E-08
327.17	2.970E-08	9.886E-09
327.29	1.047E-08	1.013E-08
327.42	2.970E-08	1.595E-08
327.55	1.045E-08	1.969E-08
327.67	1.664E-08	1.125E-08
327.79	ND	6.882E-09

327.92	8.320E-09	8.668E-09
328.04	1.951E-08	1.202E-08
328.17	8.746E-08	2.703E-08
328.29	ND	2.068E-08
328.54	7.050E-09	2.755E-08
328.67	4.265E-08	2.056E-08
328.83	1.779E-08	2.551E-10
328.92	4.237E-08	1.197E-08
329.17	1.040E-08	1.213E-08
329.29	2.622E-08	1.041E-08
329.42	ND	1.115E-08
329.54	2.478E-08	2.009E-08
329.67	2.217E-08	8.465E-09
329.79	ND	7.578E-09
329.92	1.435E-08	6.806E-09
330.04	8.300E-09	1.257E-08
330.17	5.350E-09	1.341E-08
330.29	5.800E-09	7.446E-09
331.17	ND	2.848E-08
331.29	1.380E-08	2.533E-08
331.54	3.900E-09	1.516E-08
331.67	8.300E-09	2.548E-08
331.79	3.044E-08	1.912E-08
331.92	3.676E-08	1.185E-08
332.04	1.811E-09	5.926E-09
332.17	5.029E-08	5.864E-09
332.29	1.158E-08	8.515E-09
332.42	2.269E-08	8.453E-09
332.54	ND	8.297E-09
332.67	ND	6.550E-09
332.79	ND	9.139E-09
332.92	3.506E-08	4.679E-09
333.04	1.120E-08	6.903E-08

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## REPORT 4: UNDERWAY MEASUREMENTS OF $p\text{CO}_2$ , OXYGEN AND TOTAL GAS PRESSURE

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Land, rivers, atmosphere, sediments and biota play a role in coastal ocean and shelf sea biogeochemical cycling of carbon. All these processes lead to highly variable (spatial and temporal) systems. Even if the area of coastal systems is small compared to the open ocean it plays an important role in the global carbon budget. The amount of carbon being fixed or released in coastal systems is still a number of debate [Chen and Borges, 2009] because of its high variability. The South China Sea is a poorly understood marginal sea in terms of its biogeochemistry [Morton and Blackmore, 2001]. Its circulation pattern is influenced by the Monsoon system. During winter the surface flow of the South China Sea is driven by the Northwest Monsoon and creates an anti-clockwise circulation pattern. This results in a northeasterly flow along the coast of Borneo and Philippines. Only in the near vicinity of the coast of Borneo the surface flow could reverse in southwesterly direction.

### Measurements

During SO218 cruise underway measurements of  $p\text{CO}_2$ , dissolved oxygen and gas tension were conducted. All sensors were deployed in a bath (Coleman® cooling container) that was flushed with the seawater at a typical flow rate of  $10 \text{ L min}^{-1}$ . The instruments were fed with a seawater flow from a submersible pump that was installed in the ships moonpool ( $\sim 5 \text{ m}$  depth). Sea surface salinity (SSS) and temperature (SST) were taken from the ships thermosalinograph.

$p\text{CO}_2$ : For the determination of  $p\text{CO}_2$  a submersible sensor was used (HydroC- $\text{CO}_2$ ). A flat silicone membrane acts as an equilibrator between the seawater and the inner gas volume of the sensor. The  $\text{CO}_2$  concentration in the air circuit is measured by means of NDIR detection. The sensor was calibrated before the cruise and zero values were used to account for a possible drift of the sensor following the recommendations of Fietzek et al. [2013].

Dissolved Oxygen: Dissolved Oxygen was determined with an oxygen optode (Aanderaa Instruments AS, Bergen, Norway). This technique is based on dynamic luminescence quenching. The raw data were calibrated by applying a temperature and oxygen dependent calibration polynomial that was recorded before the cruise [Bittig et al., 2012].

Gas Tension: The PSI-GTD-Pro (Pro-Oceanus Systems Inc., Halifax, Canada) measures the total dissolved gas pressure of all gases. A small sample volume of air is equilibrated to all dissolved gases in the water through a special membrane. The GTD was also installed in the water bath.

### Results

Fig. 1 shows SSS and SST along the cruise track. The study area can be divided into two parts. A part along the coast of Borneo with lower salinity values but higher variability and the Sulu Sea with higher values but lower variability. The Sulu Sea shows more open ocean condition as it is also deeper than the section along the coast of Borneo. Between  $112$  and  $113^\circ\text{W}$  salinity values fall even below  $29$  what might be caused by river runoff.

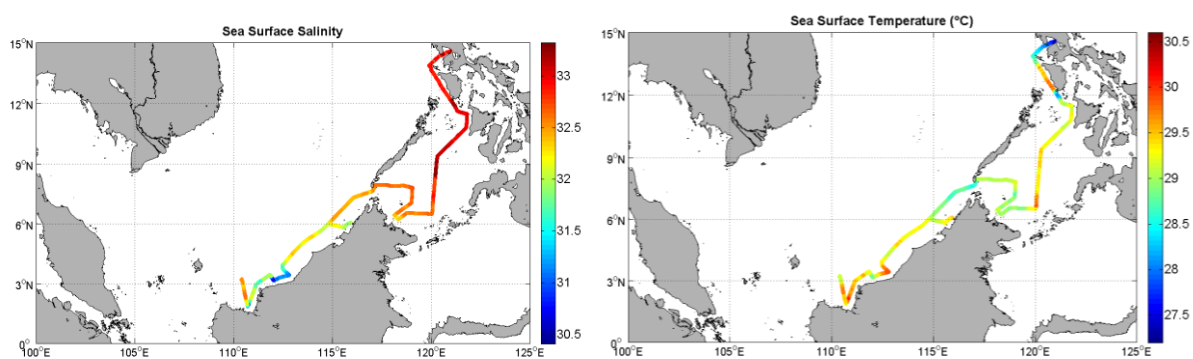
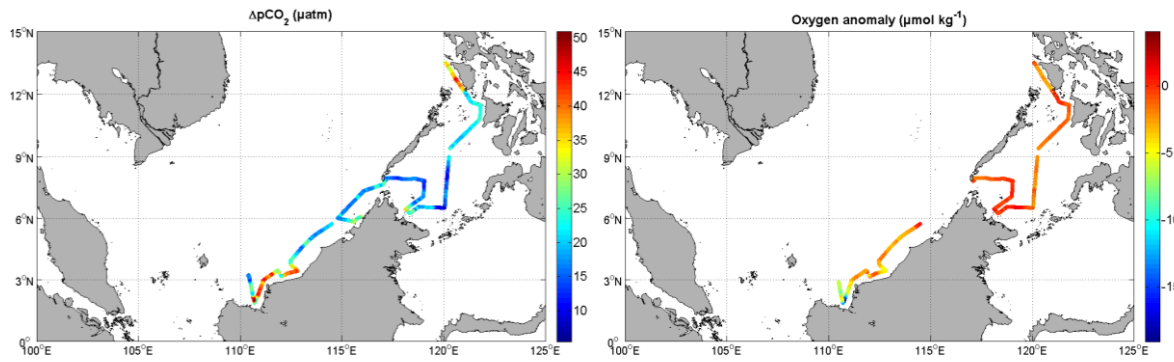


Figure 1: Sea Surface Salinity and Temperature along the cruise track of SO218.



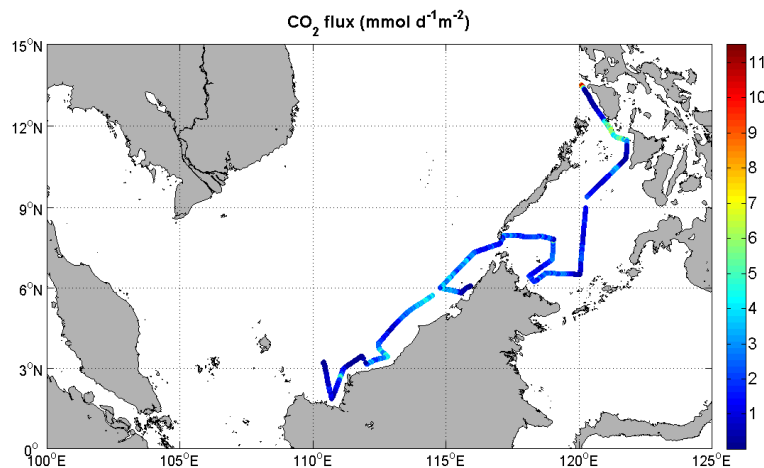
For atmospheric  $x\text{CO}_2$  data we used data from station SCSN09-01 from the Globalview network [GLOBALVIEW-CO<sub>2</sub>, 2011]. These data were used to calculate the  $p\text{CO}_2$  difference between ocean and atmosphere ( $\Delta p\text{CO}_2$ ). Fig. 2 shows the  $\Delta p\text{CO}_2$  values and the oxygen anomaly what is the difference between the observed oxygen concentration and the saturation concentration (calculated from SST and SSS). Positive values mean an oversaturation and vice versa. CO<sub>2</sub> is oversaturated during the whole cruise track with maximum values at the coast of Borneo and the Philippines. The oversaturation at the coast of Borneo coincides with the salinity minimum. Again this might be due to river runoff, as riverine water transports huge amounts of inorganic and organic carbon into the coastal ocean. The organic carbon is respired and CO<sub>2</sub> increases. This can be also observed in the oxygen data, as along the coast of Borneo oxygen is slightly undersaturated.



**Figure 2:  $\Delta p\text{CO}_2$  and Oxygen anomaly.**

The observed oversaturation of CO<sub>2</sub> is in good agreement with the data of [Rehder and Suess, 2001] who measured CO<sub>2</sub> in the same region in 1994. Using the ship's wind speed data we calculated the CO<sub>2</sub> flux  $F$  for the dataset:

where  $k$  is the wind speed dependent transfer coefficient that was calculated following the parameterization of Nightingale *et al.* [2000]. Fig. 3 shows the calculated flux values for CO<sub>2</sub>. Even if there were high concentration gradients between the ocean and the atmosphere only minor fluxes were observed during most of the cruise track due to low wind speeds. However these fluxes compare well with the results of Zhai *et al.* [2005] showing the South China Sea is a CO<sub>2</sub> source.



**Figure 3: CO<sub>2</sub> flux along the cruise track. Positive values mean a flux from the ocean to the atmosphere.**

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## REPORT 5: SHIVA SONNE SO218: RADIO- AND OZONESOUNDING

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### Scientific background

Although the first signs of the ozone recovery have been recognized in the upper stratosphere since the beginning of 2000 (WMO, 2007), still unexpected high ozone loss is eventually reported over polar latitudes since then, i.e. the record ozone loss over Antarctica in 2006 und more recently the first “Arctic ozone hole” during the winter 2010/2011 (Manney et al., 2011 *Nature*). Especially the timing of full ozone recovery in the Northern hemisphere (NH) is quiet uncertain due to the high natural variability of stratospheric temperatures during winter and the impact of naturally produced halocarbons chemical compounds, which are yet not adequately addressed in current ozone projections for the 21st century (SPARC CCMVal 2010; WMO, 2011; Manney et al., 2011 *Nature*).

Despite the well known threat of anthropogenic produced halo fluorocarbons (HFCs) on the ozone layer, very short-lived substances (VSLS) as bromine and iodine compounds and other natural trace gases have to be considered for the ozone depletion as well. These chemical species are produced in the ocean, probably through the metabolism processes of microorganisms called phytoplankton. To better understand the relationship between marine biochemistry and atmospheric chemistry and physics our SO218 SONNE expedition aims to investigate these relations into more detail. The tropical Western Pacific is especially suitable for these VSLS-transport examinations for two reasons: First, the tropical West Pacific is known to be a source region for halocarbons and has not yet been examined especially the southern part of the South China Sea. Second, this region exhibits strong convective activity throughout the year. Thus, active gas exchange between the marine boundary layer and the stratosphere (altitudes: 17-50 km), where the protective ozone layer exists. Regular (6-hourly) weather balloons are launched to improve the global meteorological assimilations, which are used as input data for trajectory and chemical transport calculations within SHIVA project, starting from the ocean surface well into the stratosphere. The ozonesonde measurements should detect direct chemical effects of the halocarbons or other chemical relevant trace gases in the atmosphere along and above our ship track.

### Scientific goals

From the SO218-SONNE expedition we derived new results concerning the atmospheric structure and content over the southern part of the South China Sea from the marine boundary layer well into the stratosphere. Given that the expedition cruised well within the tropical belt, we do not expect high variations in the meteorological parameters. Along the ship cruise from 1° N to 15° N deeper cold point temperatures within the Tropical Tropopause Layer (TTL) should be measured during November compared to boreal transition or summer seasons. Given that the cruise takes place in November starting in Singapore, we expect to be close to the Inner Tropical Convection Zone (ITCZ) with enhanced convective activity. The radiosounding of temperature, wind, humidity and ozone are used to validate the meteorological input data and serve as a starting point for the trajectory calculations with the Lagrangian dispersion model FLEXPART.

### Measurements

We have carried out 6-hourly radiosoundings of temperature, wind, and humidity, using 350 gr balloons inflated with roughly 25 kbar Helium. This routine observational program was carried out with DFM-09 radiosonde from GRAW. These radiosondes are characterized by their small lightweight package and easy handling which bears great advantage on an expedition that does not provide dedicated balloon filling and launching facilities. Also, the ground receiver equipment (antenna, radio

data acquisition) was made available at no cost from the Germany Weather Service (DWD) in Lindenberg and could be easily installed on the vessel.

Ozone sondes were launched along the western and northern coast of Borneo usually at 19 LT (11 UTC) together with a GRAW radiosonde (DFM-97), using a TOTEX balloon with 1200 gr weight and about 80 kbar Helium filling. In total 6 ozone sondes were started during our South China Sea passage as well as more 73 radiosondes. For the ozonesonde launch a DFM-97 radiosonde was tight together with the ozone instrument equipped with a 30 m enroller. These large balloons had to be filled in on deck. In order to avoid premature burst of the balloons during filling, a special cover net (“balloon launcher”) was used for protection. The balloons and the balloon launcher were produced by the Japanese company TOTEX. The balloon launches were greatly supported by the scientists and the ship crew by securing the filling and launching equipment on deck. The balloons reached frequently altitudes above 25 km. Only one small balloon burst just before starting off due to the narrow passage between the fill-in and another 20 feed container. The individual starts of the two described instruments are listed in the appendix.

## Results

The atmosphere along our trip showed throughout tropical character with minimum temperatures reaching below  $-85^{\circ}\text{C}$  around 17 km altitude (90 hPa), marking the lower boundary of the stratosphere (Figure 1 left). The tropical wind regime in the stratosphere the Quasi Biennial Oscillation (QBO) is in its Easterly phase above  $\sim 23$  km altitude (50 hPa) (Figure 1 bottom).

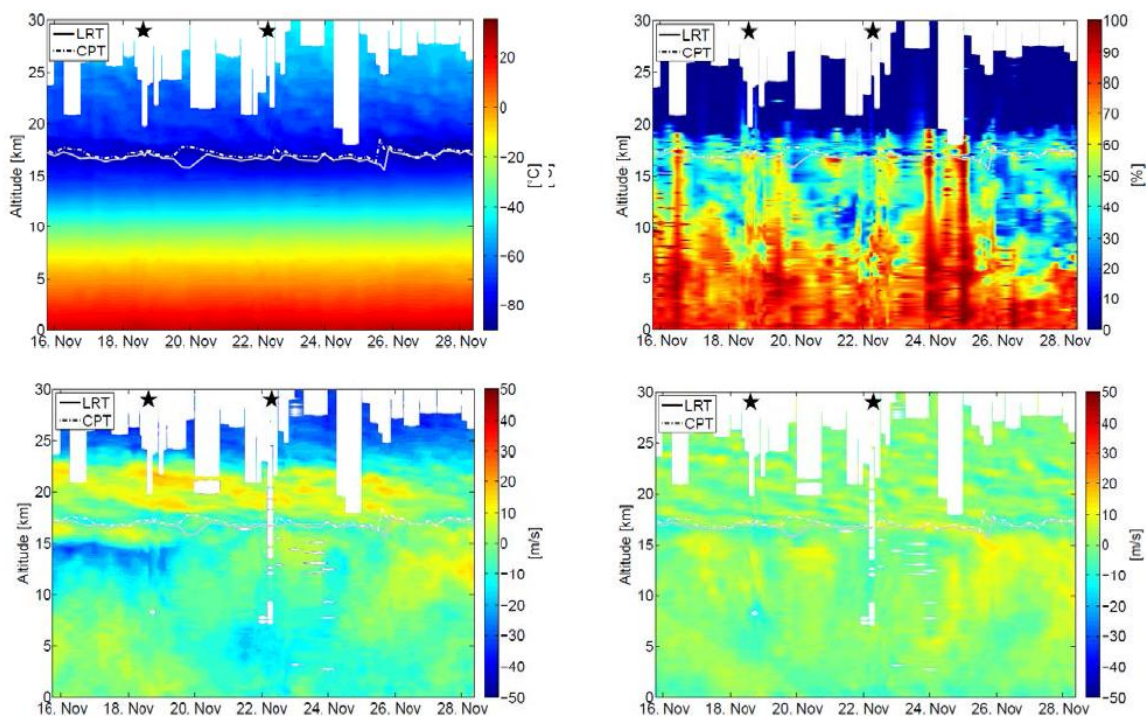


Figure 1: Profiles obtained from the radio sounding: Left: Temperature ( $^{\circ}\text{C}$ ), the dashed line shows the cold point temperature (CPT) and the solid line displays the lapse rate temperature (LRT); Right: Relative humidity (in %); Bottom: zonal and meridional wind components (m/s).

Surface winds were dominantly North Easterlies with maximum wind speeds reaching regularly above 10 m/s, the typical trace winds (Figure 2 top). Surface air temperature varied between maximum  $29^{\circ}\text{C}$  minimizing up to  $26^{\circ}\text{C}$  (Figure 2 bottom). Sea surface temperatures (SSTs) stayed above  $29^{\circ}\text{C}$  most of the time, which may be influenced by the La Nina in the tropical West Pacific. Enhanced convective activity with thunder storms and lightning occurred in Singapore and at the Northwestern tip of Borneo (Figure 3). The ozone profiles revealed low tropospheric ozone values between 15 to 70

ppb, which were however higher than the observed very low ozone mixing ratios (<10 ppb) detected during the TransBrom Sonne cruise, which crossed the tropical West Pacific further to the East (not shown here).

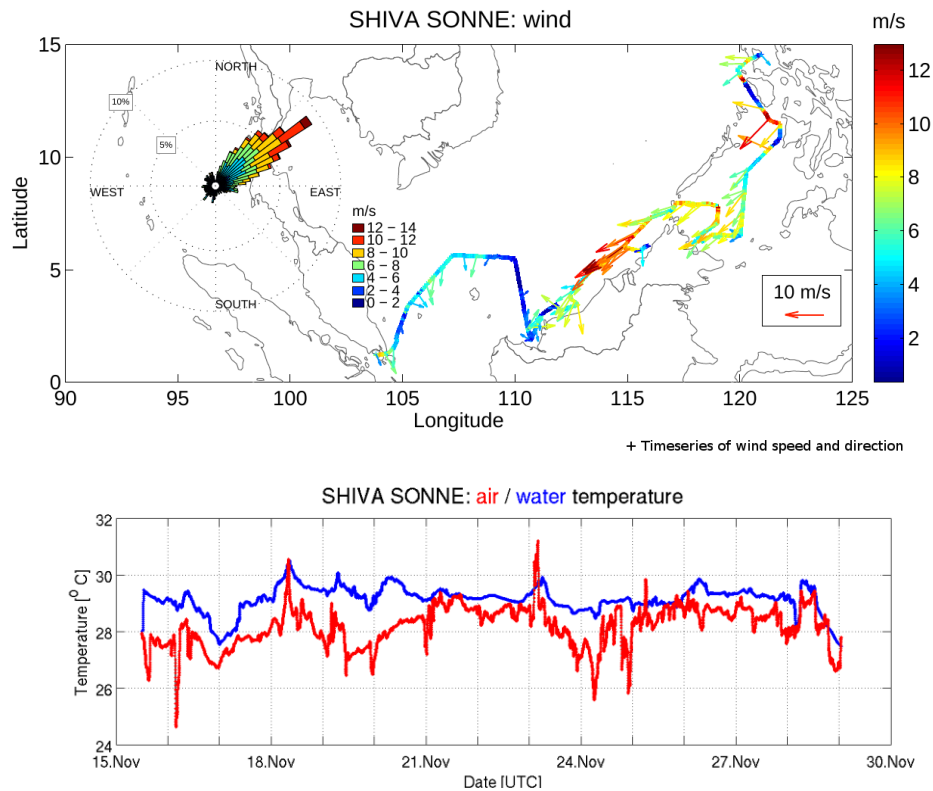


Figure 2: Top panel: wind speed (m/s) and direction; bottom panel: air and water temperature (°C) measured on board of RV SONNE during the SO218 cruise.

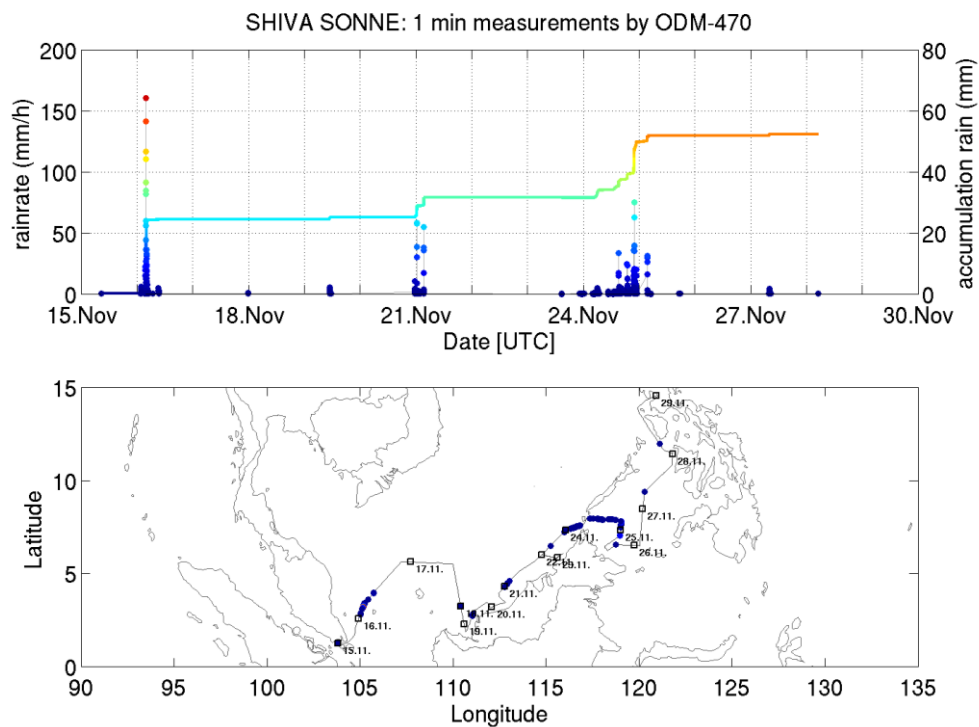


Figure 3: Precipitation measurements: rain rate (mm/h) and accumulation rain (mm).

Tegtmeier et al. (2013) analysed the air mass pathways (trajectories) from the surface into the stratosphere. With the trajectory model FLEXPART we found that the entrainment of methyl iodide into the stratosphere is projected to be higher above the tropical West Pacific than available aircraft observations showed so far. However, these aircraft measurements mainly took place in the East Pacific/ Central America. In another study the air mass exchange of VSLS through the marine boundary layer to the free troposphere is examined along the cruise and is compared with the SHIVA FALCON aircraft measurements (Fuhlbrügge et al. in preparation).

## References:

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## REPORT 6: DETERMINATION OF TRACE GAS CONCENTRATIONS IN THE MARINE BOUNDARY LAYER

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### Measurements

200 Canister air samples were taken for GC/MS- Analysis of trace gases in Miami. The air samples were taken three hourly and the sampling frequency was increased to 1 sample per hour at the diurnal stations and close to the northern coastal Borneo, where we expected interesting diurnal patterns as well.

### Results

The wind observations already reveal two different air mass origins (Figure ). From 15.11. – 19.11.2011 the mean wind speed accounts  $3.7 \pm 1.8$  m/s with a northern wind direction, while the wind changes to Northeast after 20.11.2011 until 29.11.2011 and increases to a mean wind speed of  $6.4 \pm 3.0$  m/s (Figure 1, Report No. 5). Thus, the dominating wind regime at the South China and Sulu Seas is the trade wind regime. This is reflected by an overall mean wind direction of Northeast ( $50^\circ - 60^\circ$ ) and a mean wind speed of  $5.5 \pm 2.9$  m/s. From 18.11. – 19.11.2011 the wind direction changes additionally to West before the ship reaches the coast of Kuching.

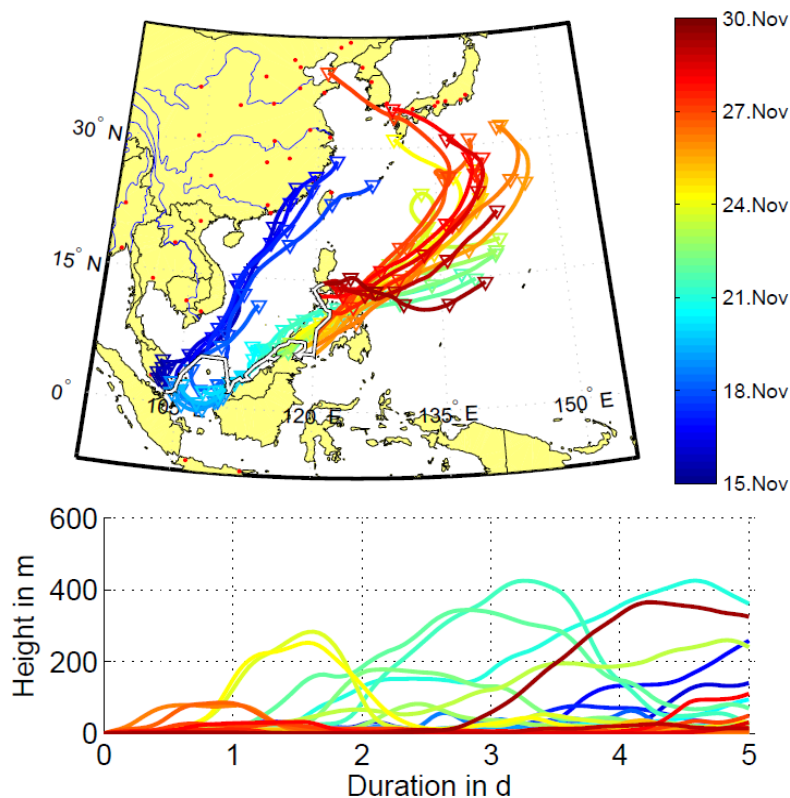


Figure 1: 5-day backward trajectories starting at the surface, meteorological input data NCEP/NCAR Reanalysis Data 1.



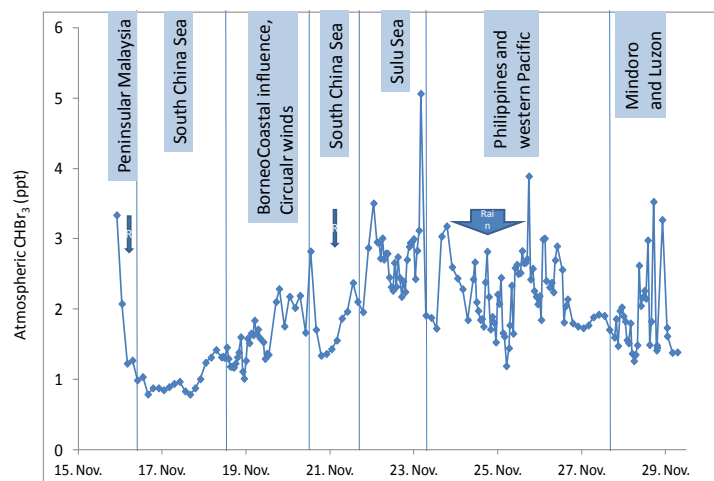


Figure 2: Origin of air-masses, determining the atmospheric mixing ratios of bromoform.

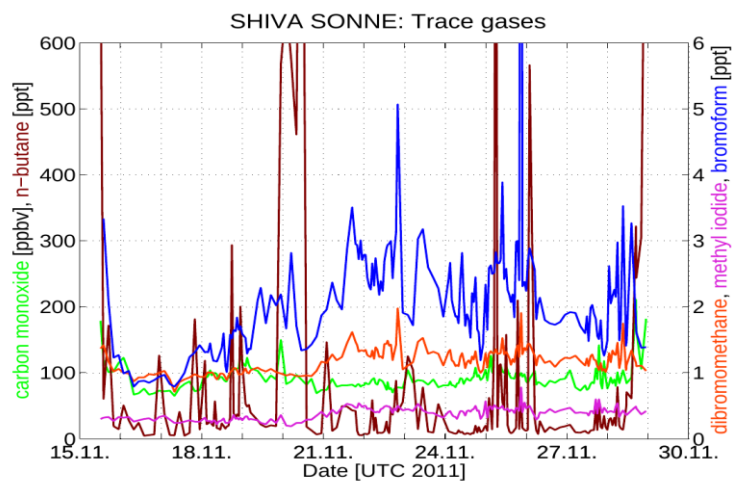


Figure 3: Anthropogenic and natural trace gases in the atmosphere of the South China and Sulu Sea.

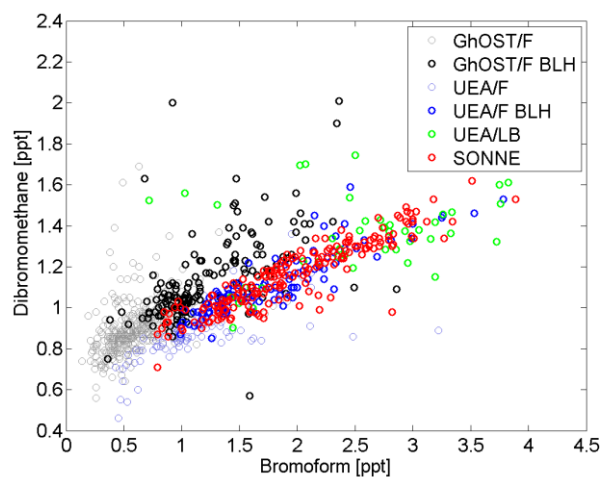


Figure 4: Bromoform vs. Dibromomethane volume mixing ratio (ppt).

**REPORT 7: TRACE GAS MEASUREMENTS USING MAX-DOAS AND CE-DOAS INSTRUMENTS**

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**Motivation**

Reactive halogen species (RHS) are known to play an important role in the troposphere as well as in the stratosphere by, among other processes, catalytically taking part in ozone destruction, NO<sub>x</sub> and HO<sub>x</sub> cycles and thus actually influencing the oxidation capacity of the atmosphere.

They can be created by oxidizing directly emitted halogen compounds, by photolysis of VSLS emitted from the ocean or in chemical reactions upon surfaces. Iodine compounds can significantly increase ozone destruction compared to bromine compounds. Additionally eventually form aerosol particles via self-reactions.

MAX-DOAS measurements provide the possibility of calculating trace gas profiles. It is possible to measure RHS as well as providing NO<sub>2</sub>, formaldehyde, glyoxal, and SO<sub>2</sub> data at the same time. Some uncertainties of concentrations can originate from radiative transport modeling. The in-situ cavity measurements have a rather well-defined path-length and thus enable us to have additional ground measurements, even though only a few trace gas species can simultaneously be measured with one instrument due to technical limitations.

**Method**

*DOAS*: (Differential Optical Absorption Spectroscopy) is a method to detect trace gases within air by measuring light spectra, calculating optical thicknesses and finally fitting trace gas absorption cross sections known from literature to these to obtain column densities and finally mixing ratios. Differential means that Mie and Rayleigh scattering are accounted for by removing the broad band structures from the optical thickness and also reducing the trace gas cross sections to their differential part. The type and number of trace gas mixing ratios which can simultaneously be retrieved depends on the wavelength range used.

*MAX-DOAS*: (Multi AXial DOAS): This particular method uses the scattered sun light as a light source prevailing measurements during night. Due to changes in the solar zenith angle and especially by looking at different elevation angles close to the horizon results in different light paths in the atmosphere. Radiative transport models are used to obtain the actual path of light and aerosol profiles. It is then possible to calculate stratospheric abundances and tropospheric trace gas profiles up to a height of usually 2-4km at a resolution of 100-1000m.

*CE-DOAS*: (Cavity Enhanced DOAS): This method is an active method and does not rely on sunlight. By means of 2 highly reflective mirrors the actual light-path from light-source to spectrometer can be several kilometers. This value is determined using a Helium calibration to minimize Rayleigh scattering or via analysis of ringdown signals. The usable wavelength window is often limited by the mirror reflectivity and usually of the order of a few 10nm.

Trace gases within the wavelength range of the MAX-DOAS systems on SO218:BrO, IO, HCHO, HONO, CHOCHO, H<sub>2</sub>O, O<sub>4</sub>, NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, OIO, I<sub>2</sub>

Trace gases within the wavelength range of the CE-DOAS system on SO<sub>2</sub>, IO, NO<sub>2</sub>, H<sub>2</sub>O, CHOCHO

### **“Samples”**

The MAX-DOAS instruments recorded spectra during daytime from the time RV Sonne left Singapore. The Heidelberg MAX-DOAS was shut down and dismantled on the evening of November, 28<sup>th</sup>, 2011. The MAX-DOAS system from Bremen continued to measure until reaching the port of Manila around 10:00 LT on the following day. Bremen's MAX-DOAS was looking towards starboard, Heidelberg's instrument towards portside. The time resolution of profiles is about 10 to 15 minutes, the detection limit for the different trace gases depend on viewing conditions with typical values for IO of 0.8 ppt, for BrO 1ppt, and for NO<sub>2</sub> around 100 ppt.

The Cavity system was operated outside on the monkey deck portside on November 16<sup>th</sup>, 2011 and from October 19<sup>th</sup>, 2011 until it stopped measuring on November 29<sup>th</sup>, 2011 around 08:00 LT. On November 17<sup>th</sup> and 18<sup>th</sup> it had to be transported back to the lab to be cleaned and readjusted. Heavy rain together with wind from the side resulted in a small drop of seaspray on of the mirrors which had lowered the sensitivity significantly. Time resolution for single spectra was usually 30s, which results in a detection limit of about 2ppt VMR for IO (for clean mirrors). For a time resolution of around 5 minutes the best achievable detection limit for IO was 0.8ppt due to systematic problems during the evaluation.

The actual air measurements were interrupted a few times for zero air and calibration measurements. Rainfall and/or sea spray was a reason for long zero air measurements to protect the instrument.

### **Results**

The MAX-DOAS measurements of Heidelberg failed during SHIVA, even though it functioned well before during MSM18 and afterwards during SOPRAN M91. The reason for this problem was not found onboard due to the high workload operating the other MAX-DOAS and especially the CE-DOAS. The Bremen MAX-DOAS worked fine during the whole cruise

CE-DOAS data has not shown any IO mixing ratios above 0.8ppt. The detection limit has been degrading towards the end of the cruise, caused by a decrease in mirror reflectivity. In contrast to this finding fit was possible to derive from MAX-DOAS measurements small IO mixing ratios between 0.5 ip and 2 ppt and in the lowest layer (0 to 500 m) with slightly higher values in the Sulu sea. These observations are in reasonable agreement to measurements from the LIF instrument operated during SO228 by the University of Leeds.

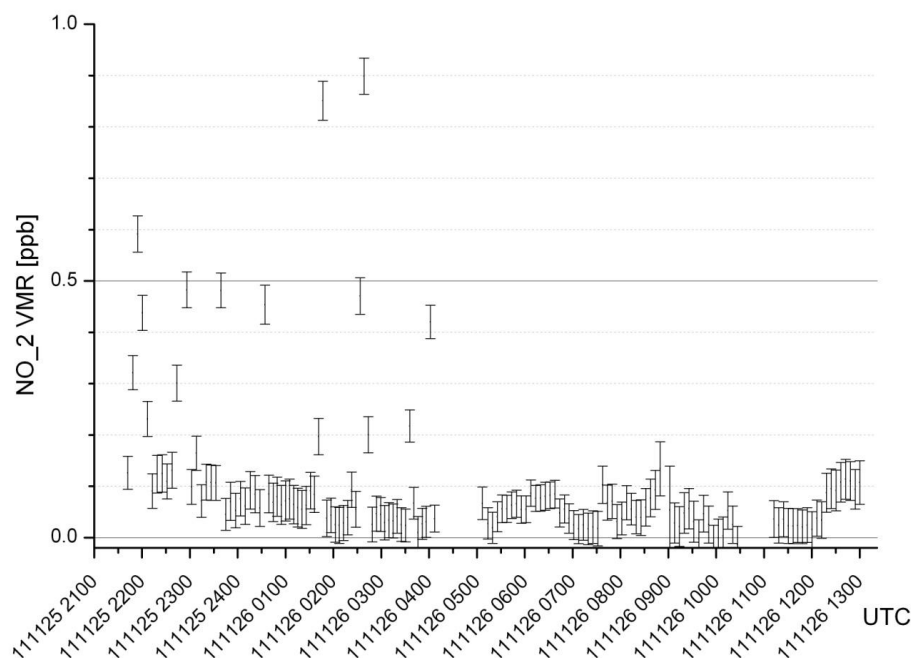
For BrO no positive detection was possible for the whole cruise.

NO<sub>2</sub> mixing ratios were also calculated and were used during the cruise to roughly estimate the influence of the ship's stack on air measurements on the monkey deck. The detection limit was usually approximately 100ppt, significantly worse during the last day approaching Manila. Direct wind from the back as well as wind from starboard seem to cause exhaust air to be mixed into air on the monkey deck. Figure1 shows six minutes averaged NO<sub>2</sub> mixing ratios and a situation with possible mixing of relatively clean air with stack air on November, 25<sup>th</sup>. Distant Sources of NO<sub>2</sub> usually appeared as broader peaks.

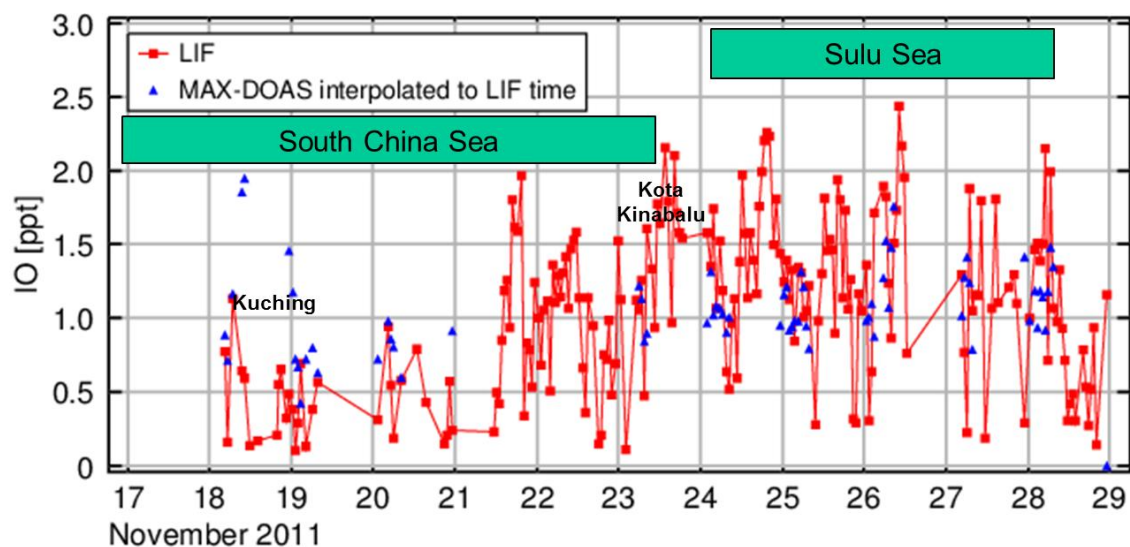
Passing through the plume of a wildfire on the Philippines on November 28<sup>th</sup>, 10-11 LT, a clear NO<sub>2</sub> signal was seen, correlating again with Ozone and CO. Glyoxal stayed below detection limit for the CE-DOAS. The Bremen MAX-DOAS was able to detect glyoxal up to 350 ppt when approaching

Manila.  $\text{SO}_2$  up to a few ppb was measured in the beginning of the cruise close to the shipping lane from Singapur through the South China Sea and occasionally during the whole cruise whenever plumes of passing ships were sampled.

Data sets both from the CE-DOAS and the Bremen MAX-DOAS can be found on the SHIVA data server.



**Figure 1:**  $\text{NO}_2$  Mixing ratios for a period where the ship exhaust might have been detected.



**Figure 2:** IO mixing ratios derived from the MAX-DOAS and from the LIF instrument.

## REPORT 8: $\mu$ -DIRAC – CONTINUOUS MEASUREMENTS OF HALOGENATED TRACE GASES

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On this cruise, one of few world-wide existing, non-commercial  $\mu$ -Diracs (micro-Dirac) was operated. Apart from being lighter in weight and less expensive compared to a conventional GC-MS system, it does not require a high degree of human operation, as it runs automatically. The focus lay on detecting short-lived halocarbons in the tropical marine boundary layer. Bromoform ( $\text{CHBr}_3$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and iodomethane ( $\text{CH}_3\text{I}$ ) were of special interest during this cruise campaign. In addition to the  $\mu$ -Dirac used for the cruise, an earlier version of the instrument was operating at the GAW station on Bukit Atur (Sabah) during the period of the SHIVA campaign.

### Methodology - The $\mu$ -Dirac

The marine boundary layer air mass measurements were performed using a gas chromatograph (GC) equipped with an electron capture detector (ECD). This so-called  $\mu$ -Dirac was designed in Great Britain and has been detecting halocarbons in New Zealand since March 2010 (before being deployed on RV Sonne). The  $\mu$ -Dirac is capable of measuring halocarbons in the atmosphere having mixing ratios lower than 1ppt (parts per trillion).

Brief description of  $\mu$ -Dirac setup: The halocarbons contained in an air sample (typical sample size: 20cm<sup>3</sup>) pass through an inlet to a Valco Valve, on top of which an adsorption/ desorption tube is situated containing two different Carboxen materials. Depending on the respective boiling points the individual halocarbons are being adsorbed by either one of the Carboxen materials.

Flash-heating of the adsorbent tube is subsequently carried out, with temperatures reaching values up to 180° C. The target compounds are readily desorbed and pass onto the separation column along with the Helium purge gas (optimal Flow rate: 0.3cm<sup>3</sup>/ min). This so-called carrier gas is purified in advance in order to remove moisture and other contaminants. Flowmeters control the helium gas (and sampling gas) flow entering the system which is essential for reproducing peak retention times.

The separation capillary column is 10 meters long (MXT-502.2), furnished with an inner wall coating and is mounted in a temperature-controlled oven enclosure made from foam board. Here, it serves as the stationary phase of the GC. Dependent on respective partial vapor pressures and temperature, the sample partitions between the mobile (Helium) and stationary phase and is separated into individual components. Each halocarbon passes through the detector at a unique speed and thus reaches the detector at a characteristic retention time which is defined as the sum of residence time within the mobile and stationary phase. A whole sample run lasts approximately 35 minutes, depending on the column temperature.



Figure 1:  $\mu$ -Dirac deployment on RV Sonne on the scientific bridge. Photo: Julian Kinzel

The column outlet is connected to the heated detector. Target halocarbons pass into the micro-volume ECD which is highly temperature- and pressure-sensitive. Here, they are ionized within an electron field formed by ionization of a nitrogen make-up gas from primary electrons emitted from a  $^{63}\text{Ni}$  foil (acting as a beta emitter). An ionization background current is thus established and maintained at a constant level due to an electrometer. Since the halogenated compound's electron affinity is high, the current is reduced, proportional to the compound concentration. A 16 bit ATD-converter finally produces the 10Hz output which yields the final chromatogram. On the basis of retention times and corresponding peak heights, one can identify numerous halocarbons and convert the signal into ppt-volumes by referring to separately conducted calibration runs.

### **$\mu$ -Dirac - Deployment on RV Sonne**

The  $\mu$ -Dirac was deployed on the scientific bridge (see Fig.1), where access to the outside was provided for the sampling tube. The outside-end of the tube was attached to a reeling on the port side of the monkey deck. An attached funnel prevented too much moisture from entering the system. This sampling spot was chosen to avoid the influence of the ship's exhaust, which was situated further 'downwind'. The Helium and Nitrogen cylinders were installed outside of the scientific bridge and connected to the  $\mu$ -Dirac via stainless steel tubes.

Air samples were taken approximately once every 45 minutes, thus allowing for a relative high measurement frequency throughout the cruise (i.e. roughly 18 air samples per day). Calibrations and blank runs were conducted every 4 hours, respectively. Apart from focusing on bromoform, dibromomethane and iodomethane, the analysis also comprised ppt-concentrations of chloroform ( $\text{CHCl}_3$ ), PCE ( $\text{C}_2\text{Cl}_4$ ), chloriodomethane ( $\text{CH}_2\text{ClI}$ ) and dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ). Due to installation issues, reliable real time data is not available until several hours after departing from Singapore. Measurements were taken until the arrival in Manila, i.e. the morning hours of November 29th.

## Results

The results show, that there is qualitative agreement between the air concentrations measured in the air canister and the  $\mu$ -Dirac (Figures 2 to 6). Differences may be the result in the time resolution of the measurements, the general offsets are likely the results of calibration differences while extreme outliers, e.g. for methyl iodide can't be explained by those reasons.

Concentrations of bromoform ( $\text{CHBr}_3$ ) vary between 1-5 ppt (Figure 2). Higher values tend to be observed close to the coast (e.g. 113/114°E) and near Kuching (111° E), especially when the persisting wind direction had a considerable off-land component. Extraordinarily large concentrations (e.g. greater than 10ppt) were not observed.

Dibromomethane concentrations ( $\text{CH}_2\text{Br}_2$ ) tend to be slightly lower than those of bromoform (generally 0.3-1.5 ppt) (Figure 3). Regions characterized by elevated  $\text{CHBr}_3$  levels (see above) also resolve relatively high dibromomethane concentrations. Overall, levels prior to cruising near Kuching were considerably smaller than during the second week of the cruise.

Methyl iodide concentrations ( $\text{CH}_3\text{I}$ ) generally remained below 1.5 ppt (Figure 4). Again, highest values occurred in the coastal areas (exception in the open sea near 110°E). Temporal and spatial variability is especially evident during the second local boat contact.

Chloroform ( $\text{CHCl}_3$ ) ppt's varied between 8-14 ppt throughout the cruise (Figure 5). During the first week of the cruise, it seems as if a multi-diurnal cycle of  $\text{CHCl}_3$  concentrations occurred. However, this structure was not reproduced during the last days of the cruise.

A time series of PCE ( $\text{C}_2\text{Cl}_4$ ) mixing ratios showed an exponential decrease within the first days (starting with roughly 7 ppt) of the cruise and remaining rather constant (1-2 ppt), once fresh anthropogenic impact became negligible ( Figure 6).

The data were calibrated based on the pre- and post-cruise analysis of the decanted NOAA calibration gas, against the NOAA SX standard cylinder in the UCAM lab.

The pre-cruise comparison of the Sonne calibration was done straight after decanting from the main NOAA-SX standard can. This showed changes in the composition of the decanted can as follows:  $\text{CH}_2\text{Br}_2$  fell by ~0.2 ppt (~ 7 % fall),  $\text{C}_2\text{Cl}_4$  fell by ~0.3 ppt (~15 % fall),  $\text{CH}_3\text{I}$  fell by ~0.1 ppt (~ 4 % fall),  $\text{CHCl}_3$  rose by ~0.6 ppt (~ 7 % rise),  $\text{CHBr}_3$  fell by ~0.3 ppt (~ 6 % fall)

After the cruise the decanted cal was again measured against the original NOAA SX can and the following changes in composition inside the decanted can were found:  $\text{CH}_2\text{Br}_2$  fell by ~0.3 ppt (~14 % fall),  $\text{C}_2\text{Cl}_4$  rose by ~0.3 ppt (~13 % rise),  $\text{CH}_3\text{I}$  rose by ~0.3 ppt (~ 9 % rise),  $\text{CHCl}_3$  fell by ~0.6 ppt (~ 7 % fall),  $\text{CHBr}_3$  rose by ~0.1 ppt (~ 1 % rise)

These changes were applied to the cruise samples based on linear interpolation between the pre- and post-cruise calibration dates and the mid-date of the cruise.

The changes to the cruise samples are not huge as can be seen in the time series plots. The error bars in the plots are the 1-sigma cruise precision from the onboard cals:  
 $\text{CH}_2\text{Br}_2$  12 %,  $\text{C}_2\text{Cl}_4$  13 %,  $\text{CH}_3\text{I}$  14 %,  $\text{CHCl}_3$  15 %,  $\text{CHBr}_3$  16 %

The estimated 1-sigma accuracy based on the NOAA uncertainty and those from our pre and post-cruise calibrations are as follows (not included in the plot error bars):  
 $\text{CH}_2\text{Br}_2$  10 %,  $\text{C}_2\text{Cl}_4$  8 %,  $\text{CH}_3\text{I}$  16 %,  $\text{CHCl}_3$  7 %,  $\text{CHBr}_3$  9 %



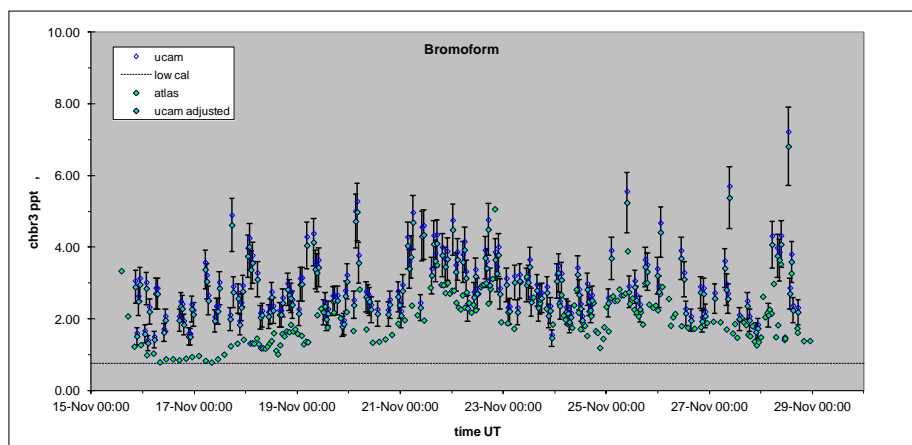


Figure 2: Atmospheric mixing ratios of bromoform (CHBr<sub>3</sub>) of canister samples from RSMAS (atlas), and  $\mu$ -dirac data (ucam and ucam adjusted to postcruise calibration).

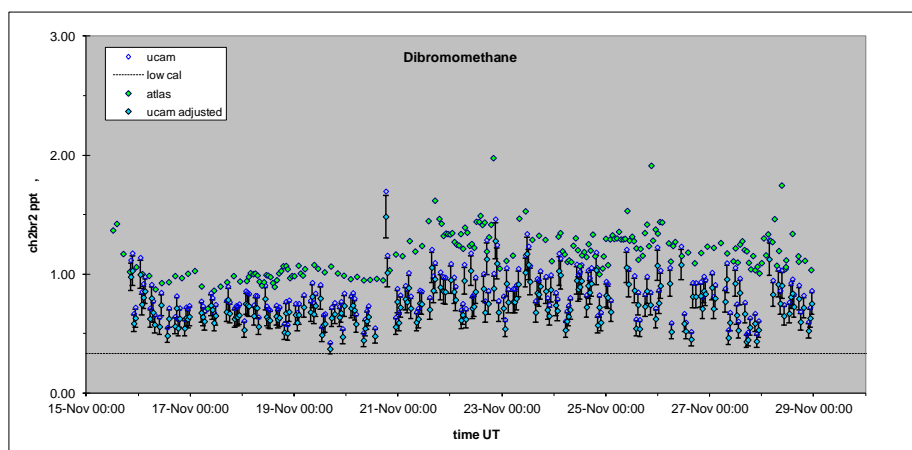


Figure 3: Atmospheric mixing ratios of dibromomethane (CH<sub>2</sub>Br<sub>2</sub>) of canister samples from RSMAS (atlas), and  $\mu$ -dirac data (ucam and ucam adjusted to postcruise calibration).

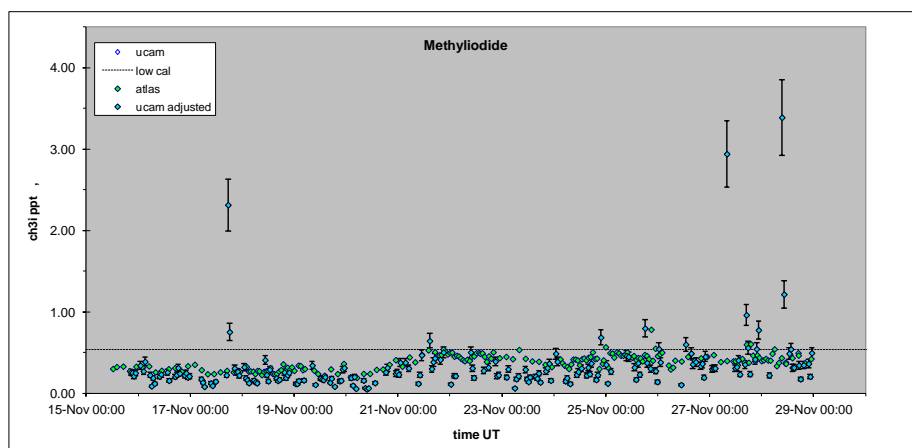


Figure 4: Atmospheric mixing ratios of methyl iodide (CH<sub>3</sub>I) of canister samples from RSMAS (atlas), and  $\mu$ -dirac data (ucam and ucam adjusted to postcruise calibration).

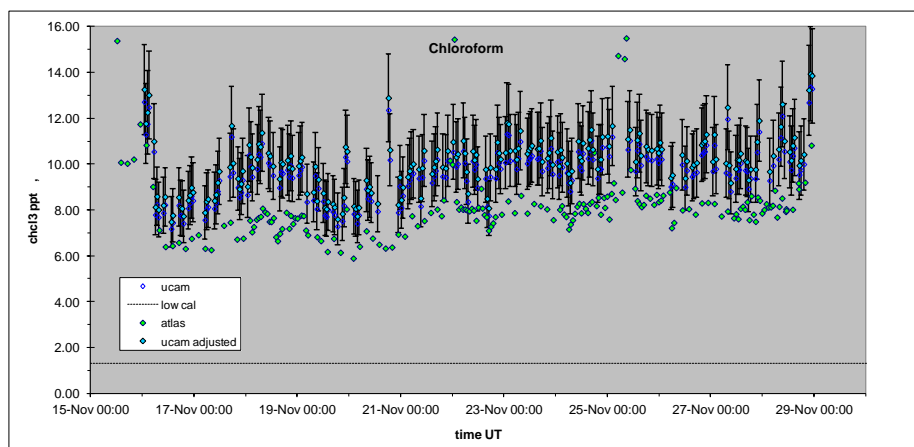


Figure 5: Atmospheric mixing ratios of chloroform ( $\text{CHCl}_3$ ) of canister samples from RSMAS (atlas), and  $\mu$ -dirac data (ucam and ucam adjusted to postcruise calibration).

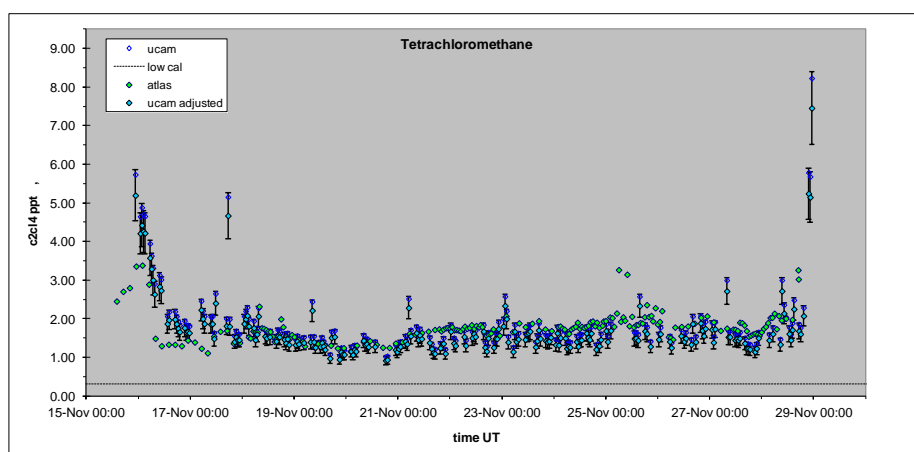


Figure 6: Atmospheric mixing ratios of tetrachloroethene ( $\text{C}_2\text{Cl}_4$ ) of canister samples from RSMAS (atlas), and  $\mu$ -dirac data (ucam and ucam adjusted to postcruise calibration).

## REPORT 9: CONTINUOUS MEASUREMENTS OF THE ATMOSPHERIC MIXING RATIOS OF A SUITE OF POLLUTION INDICATORS AND GREENHOUSE GASES (CO, CH<sub>4</sub>, O<sub>3</sub>, CO<sub>2</sub>)

Expeditioner: Justin Sentian / Nur Aleesha Abdullah, UMS, Kota Kinabalu, MMD Malaysia

Principle investigator: Hans Schlager (DLR, not on board)

### 1.0 Objective

- To measure carbon monoxide and tropospheric ozone levels and to investigate spatial and temporal variability in lower tropical marine boundary layer.
- To measure greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O) levels and to investigate spatial and temporal variability in lower tropical marine boundary layer.

However, due to the technical problem with the Picarro instrument, the measurement of the greenhouse gases was halted and therefore no greenhouse gases data were obtained during this campaign.

### 2.0 Method

In general, the 3 instruments namely TE49 Ozone Analyzer, Carbon Monoxide Analyzer and Picarro is being mounted to two racks and placed at the scientific bridge on-board the RV Sonne. All the inlets of the instruments are integrated into only one main inlet which is connected to the ambient air at the top of the Scientific bridge through the ducting system.

The setup of the whole instrument at the scientific bridge of the RV-Sonne is shown in Figure 1

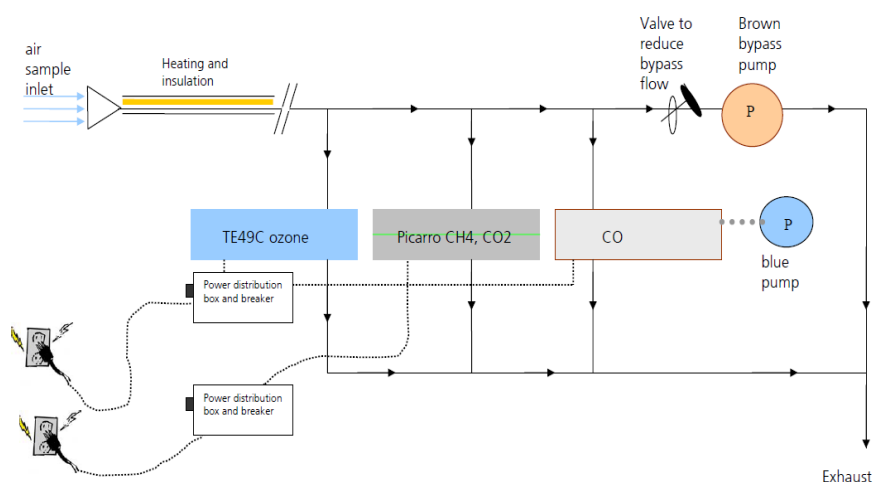


Figure 1: The instrument setup on-board RV-Sonne

Table 1: Instrument and operating status

Instrument	Parameter	Operation Principle
Model 49C UV Photometric Ozone Analyzer	O <sub>3</sub>	UV absorption at 254 nm
Model AL 5001 CO-Monitor	CO	Non-Dispersive Infra-Red (NDIR)
Picarro G1301 Analyzer ( not operational)	CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O	Optical absorption spectroscopy – based on wavelength-scanned cavity ring down spectroscopy (WS-CRDS)

## REPORT 10A: DLR- CIMS MEASUREMENTS: INVESTIGATION OF ANTHROPOGENIC EMISSIONS AFFECTING AIR QUALITY IN THE MARINE BOUNDARY LAYER OF THE SOUTH CHINA AND SULU SEA

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Measurements of reactive chlorine and bromine compounds in the marine boundary layer in the Western Pacific are rare. Reactive halogen compounds like  $\text{Br}_2$ ,  $\text{BrCl}$ , and  $\text{Cl}_2$  evolve from sea spray aerosol. Strong acids like  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ , which are secondary products of anthropogenic combustion processes, change the acidity of the sea spray aerosol. Through acid displacement the release of reactive halogen species can be enhanced. Furthermore,  $\text{Br}_2$  and  $\text{BrCl}$  evolve from  $\text{HOBr}$  by heterogeneous reactions on sea salt aerosol. Both are photolysed during the day and react with  $\text{O}_3$  to form  $\text{BrO}$ . As a consequence MBL ozone is destroyed in a catalytic cycle. Apart from sea spray aerosol very short lived substances (VSLs) may be an important source for reactive bromine compounds in the MBL. However, their contribution is highly uncertain.

In polluted coastal regions elevated concentrations of  $\text{ClNO}_2$  have been measured.  $\text{ClNO}_2$  is a night-time reservoir for chlorine and active nitrogen oxides. After sunrise photolyses of  $\text{ClNO}_2$  slowly releases  $\text{Cl}$  which oxidizes methane and volatile organic compounds. Local air pollution affects public health, environmental quality, agricultural industry and it changes the oxidation capacity of the Marine Boundary Layer (MBL), thus for example the lifetime of the greenhouse gas methane ( $\text{CH}_4$ ).

For measurements of the reactive halogen compounds ( $\text{Br}_2$ ,  $\text{BrCl}$ ,  $\text{HOBr}$ ,  $\text{BrO}$ , and  $\text{ClNO}_2$ ) and as an indicator for inorganic acids ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{SO}_2$ , and  $\text{HBr}$ ) two Atmospheric chemical Ionization Mass Spectrometers, AIMS-1 and AIMS-2, were deployed inside a 10 ft container on the backdeck of the RV Sonne. This laboratory container was designed, modified, and equipped by DLR, Oberpfaffenhofen for this cruise. Furthermore, in cooperation with the University of Leeds the container was deployed with a LIF Instrument (for IO) and a  $\text{NO}_x$  detector (University of Leeds).

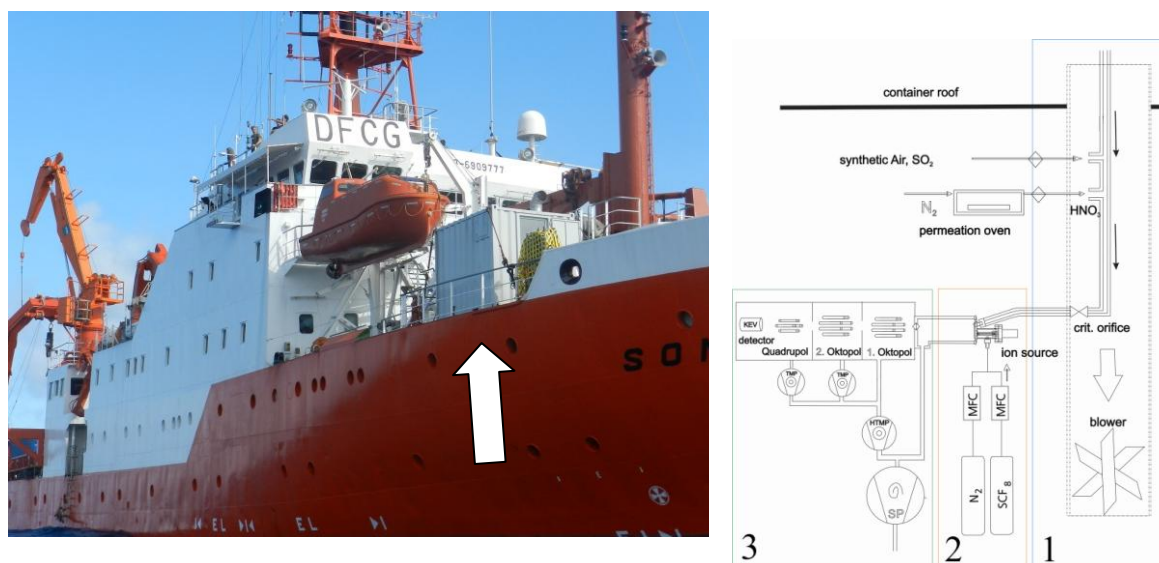


Figure 1: (left) DLR 10ft container with inlet system on the backdeck of RV Sonne. (right) Schematic setup of the AIMS instrument inside the container. Inlet (1), ionization (2) and detection region (3) are explained in the text.

AIMS-1 and -2 detect atmospheric trace gases with concentrations of a few ppt by chemical reactions with artificially produced ions ( $I^-$  and  $SF_5^-$ ) from a corona discharge ion source (Fig 1, (2)). Product and educt ions are filtered by a quadrupole mass filter (Fig 1, (3)) and individually detected by a channeltron multiplier.

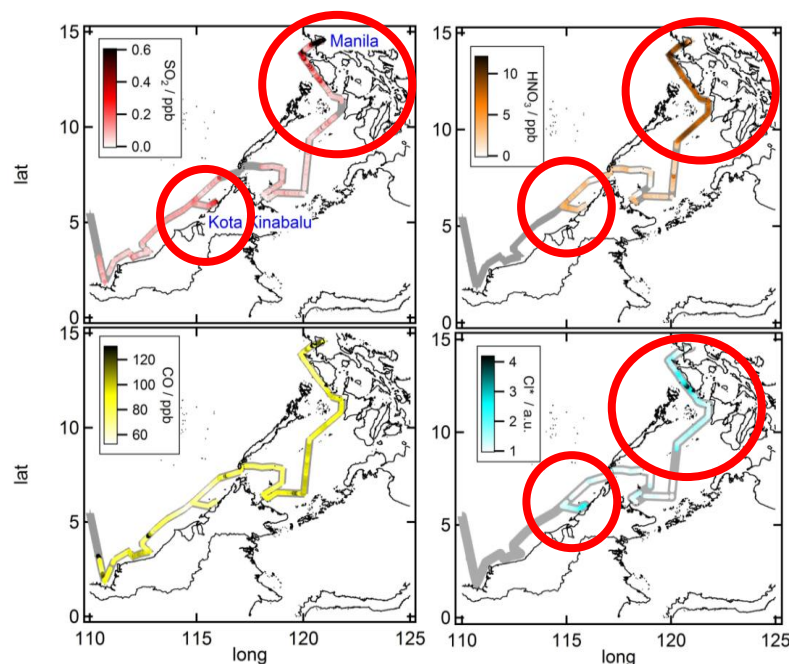


Fig 2 Atmospheric mole fractions of  $SO_2$ ,  $HNO_3$ ,  $CO$  (ppb) and  $Cl^*$ (a.u.) along the SONNE ship track. Red circles show regions with elevated concentrations along the coast of large cities.

Using the  $I^-$  reagent ions,  $SO_2$  laboratory tests showed that the detection scheme is independent of the water vapor content thus it is very suitable for measurements at high relative humidity. Permeation devices were used for calibration. Occasional gaps in the time series evolve from calibration sequences. Mass spectra with a range from 20 to 300 amu were recorded every 8 min and continuous measurements of 16 different selected masses were done with a time resolution of 8s. High sensitivity for  $SO_2$  and  $Br_2$  of 1-3 Hz / ppt were determined during the cruise.

The instruments installed on SONNE were originally designed to measure trace gas

concentrations at low mixing ratios under dry upper tropospheric conditions. Before the cruise, first extensive tests were conducted in the laboratory yielding high sensitivities and relatively low detection limits (3-10 ppt) for the components. In order to measure these components under MBL conditions additional effort was necessary to reduce high sea salt deposition on the inlet walls.

The inlet system has been adapted such that contact to the ship surface is avoided (Fig. 1, (1)). An inlet system was connected to a blower providing a large flow  $1100 \text{ m}^3/\text{h}$  through a 30cm stainless steel tube on the container roof. Air from above the ship was sampled presumably with minimal contact to the roof. In case of rain the tube was covered with a  $90^\circ$  angle piece on top of the straight inlet tube. The container was additionally equipped with two air conditioning system. Thus the instruments were operated at a constant temperature and humidity which proved to be very important at these humid conditions in the tropical sea.

With the help of a critical orifice made of PFA, the biggest part of the inlet tube was kept at low pressure to reduce the relative humidity and residence time of the gases in the inlet. A small film of salted water at the upper, inner part of the PFA inlet tubes was however unavoidable. Due to the exposed position of the container occasionally sea spray entered the inlet tubing. Cleaning of the inlet tube was therefore performed on a regular basis.

Sensitive and high-resolution sulfur dioxide ( $\text{SO}_2$ ), nitrogen oxides ( $\text{HNO}_3$ ) and active chlorine ( $\text{Cl}^*$ )(measured by AIMS) together with CO measurements (provided by E. Atlas) are shown in Fig 1. Along the cruise track both  $\text{SO}_2$  and  $\text{HNO}_3$  were elevated above the detection limit of 16 ppt. Short term pollution events from the ship stack and other close by ships were identified and separated from background measurements.

Background concentrations are 0.09 ppb ( $\text{SO}_2$ ), 0.2 ppb ( $\text{HNO}_3$ ) and 90 ppb (CO), respectively and suggest a moderately polluted MBL when compared to measurements in the remote North-Atlantic and West-Pacific MBL (e.g. Lee et al., 2010). Specifically in coastal regions near large cities such as Manila and Kota Kinabalu elevated concentrations were detected. Here, release of active chlorine (blue color coding) has been observed. This active chlorine is detected in the form of  $\text{Cl}^-$  in the mass spectrometer. The measurements support observations of halogen release due to acid displacement in the polluted MBL (Lawler et al., 2009).

Atmospheric concentrations for  $\text{Br}_2+\text{HOBr}$ ,  $\text{BrO}$ ,  $\text{HBr}$  and  $\text{ClNO}_2$  were always below the detection limit during the cruise. Partly this was due to technical problems that caused an enhanced detection limit of around 30 ppt (one sigma standard deviation). These technical problems were only observed during the cruise and have been eliminated since.

The measurements will be used for validation of the global climate model EMAC at the Institut für Physik der Atmosphäre, DLR Oberpfaffenhofen and will contribute to a better understanding of anthropogenic emissions and their effects on local air pollution.

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## REPORT 10B: SONNE- FALCON LAGRANGIAN TRACER EXPERIMENT AND CONTINUOUS CARBON MONOXIDE AND OZONE MEASUREMENTS

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A Lagrangian experiment has been performed during SHIVA using a new perfluorocyclocarbon tracer system (PERTRAS) developed at DLR (Ren et al. 2013). The Lagrangian approach is to follow a single air mass with multiple measurements and study the dispersion and change of composition as it moves. The objectives of the SHIVA experiment were to study the transport and dispersion of emissions (e.g. very short lived species) in the tropical marine boundary layer (MBL) and the handover of the emissions to the free troposphere, the comparison of the measurement data with transport model simulations, and the demonstration of this novel experimental technique. PERTRAS consists of three main modules: a tracer release unit (RU), an adsorption tube sampler (ATS) and a tracer analytical system. The tracer release unit was used on board the Sonne for release of a perfluoromethylcyclopentane (PMCP) tracer (8.8 kg) on 21 Nov 2011 near Miri, Malaysia, from 0224 to 0303 UTC. The PMCP tracer was sampled downstream of the Sonne by the DLR Falcon research aircraft with the ATS on 21 and 22 Nov. 2011 about 5 and 25 hours after the release. The Falcon sampling flights were planned using forecasts calculated with the particle dispersion model HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) driven by GSF and ECMWF meteorological forecast data.

The adsorption tube samples collected during the Falcon flights were analyzed after the field campaign in the laboratory at DLR using a thermal desorber/gas chromatography/mass spectrometry (TD/GC/MS) system. Figure 1 shows measured PMCP mixing ratios during the Falcon flight on 21 Nov 2011 along five transects through the tracer plume predicted by HYSPLIT.

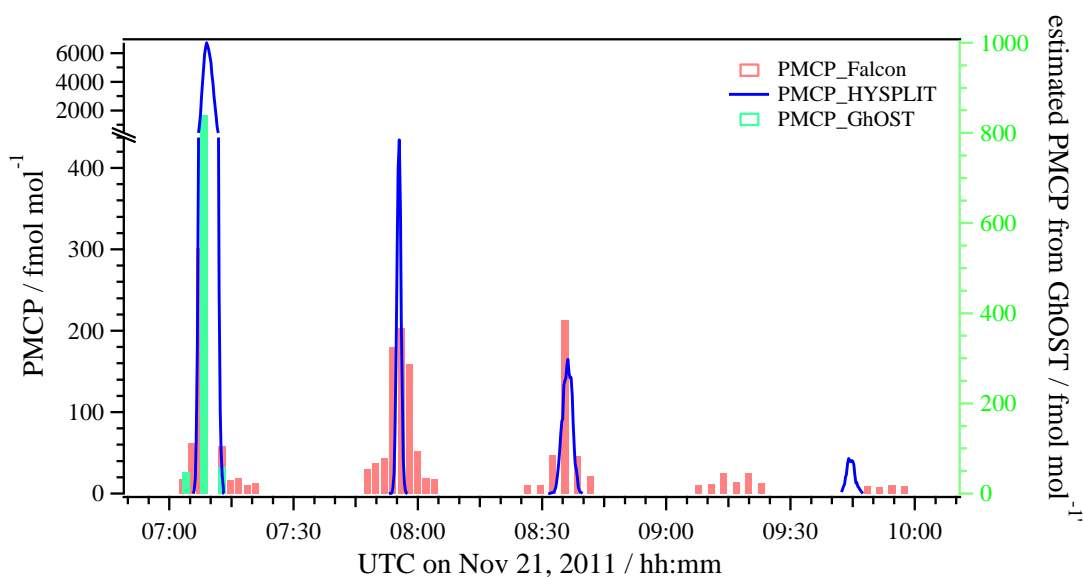


Fig. 1: Time series of PMCP tracer measurement (red bars) on November 21 and HYSPLIT simulation using GFS data (blue lines). Green bars indicate PMCP estimates from GhOST in-flight GC data.

During all five Falcon transects enhanced PMCP concentrations were detected with a maximum value of  $301 \text{ fmol mol}^{-1}$ . PMCP background mixing ratios measured outside of the tracer plume and during



other Falcon flights ranged between 5-7 fmol mol<sup>-1</sup>. During the second sampling flight on 22 Nov 2011, PMCP concentrations between 15-20 fmol mol<sup>-1</sup> were measured in the tracer plume aged 25 hours. Thus, the tracer plume has been intercepted successfully during both sampling flights. The PMCP measurements during the first three plume intercepts on 21 Nov 2013 (Fig. 1) compare reasonable with the HYSPLIT/GFS calculations, although, the simulated PMCP tracer plume is less dispersed with higher maximum concentrations. The HYSPLIT/ECMWF simulations compare worse with the PMCP tracer measurements. More details are given in Ren et al. (2013).

In addition to the Lagrangian tracer experiment continuous carbon monoxide (CO) and ozone (O<sub>3</sub>) in-situ measurements were performed during the entire Sonne cruise. The measurement techniques used were vacuum UV fluorescence and UV absorption, respectively. The CO data can be used as tracer for pollution plumes from land-based combustion sources (biomass burning, anthropogenic emissions) and shipping.

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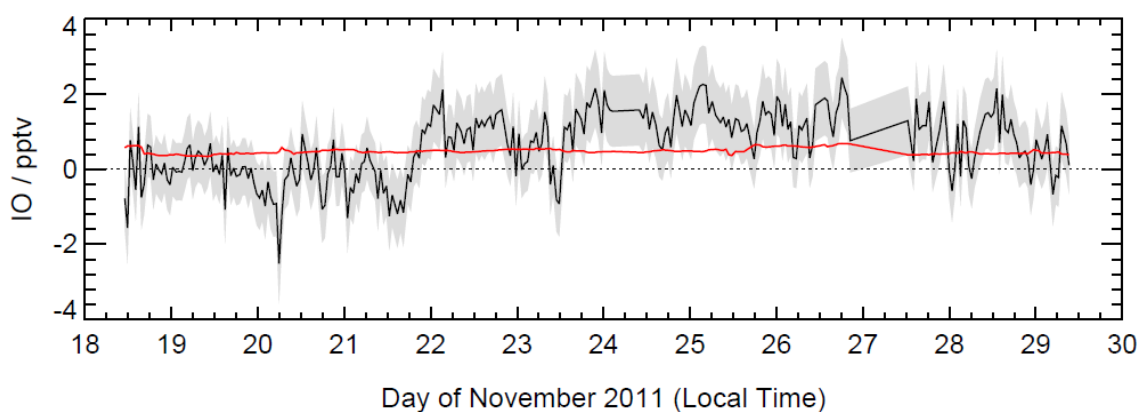
## REPORT 10C: *IN SITU* MEASUREMENTS OF IO BY LASER-INDUCED FLUORESCENCE SPECTROSCOPY

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Measurements of IO were made by the Leeds Laser-Induced Fluorescence instrument positioned on the front deck of RV *Sonne*. Ambient air was drawn through an inlet (0.8 mm diameter) into a low-pressure (150 Torr) detection chamber. Laser light at  $\lambda = 440$  nm excited the sampled IO radicals, and the resulting short-lived fluorescence at  $\lambda = 521$  nm was detected by a channel photomultiplier tube on an axis perpendicular to both the gas flow and the laser beam. Measurements of IO and the background signal were achieved by modulating the laser wavelength between an ‘online’ and ‘offline’ position, respectively. The signal was recorded every second, and the data were averaged to 15 minutes of online data, which is equal to a total averaging time of 45 minutes. The instrument was calibrated during the cruise by generating a known concentration of IO by photolysis of  $\text{N}_2\text{O}$  in the presence of  $\text{CF}_3\text{I}$ .

Mixing ratios of IO remained close to the limit of detection of the instrument ( $\sim 0.5$  pptv), with the mean mixing ratio during the cruise being 0.8 pptv. The maximum value (2.4 pptv) was observed whilst the ship was crossing the Sulu Sea to the north of Borneo. Figure 1 shows a time series of IO during the whole cruise. The IO measurements made during cruise SO218 are slightly lower than the range of values measured during a previous cruise in the Western Pacific (Großmann *et al.*, 2013) but are within the range of values measured during previous studies in other open ocean regions (e.g. Allan *et al.*, 2000, Read *et al.*, 2008, Mahajan *et al.*, 2012, Dix *et al.*, 2013, Gómez Martín *et al.*, 2013).



**Figure 1.** Time series of IO measured by LIF during cruise SO218. IO data are represented by black line, with the uncertainty in the measurements shown by the shaded grey area. Instrumental limit of detection is represented by the red line. The dotted black line indicates zero pptv. Data points below the limit of detection are shown to indicate the IO profile along the cruise.

The relationships between IO and its potential precursors have been investigated. No significant correlation was found between IO and air temperature ( $r = 0.027$ ), sea surface temperature ( $r = -0.19$ ), salinity ( $r = 0.25$ ), or wind speed ( $r = 0.28$ ), in contrast to previous studies (Mahajan *et al.*, 2012, Gómez Martín *et al.*, 2013, Großmann *et al.*, 2013), though the range of values of these physical parameters was small during cruise SO218 compared to during the previous studies. No significant

correlation ( $r = -0.17$ ) was found between IO and oceanic concentrations of chlorophyll-*a*, suggesting that there was not a strong biogenic source of reactive iodine during cruise SO218. Surprisingly, IO was found to be negatively correlated to  $I_2$  ( $r = -0.59$ ) and the sum of HOI + ICl ( $r = -0.41$ ). This relationship is as yet unexplained, though it may be explained in part by the reaction of IO with  $HO_2$  to produce HOI, and uptake of HOI to sea-salt aerosol, which releases  $I_2$  and ICl. No strong correlation was found between IO and atmospheric  $CH_3I$  ( $r = 0.26$ ), indicating that  $CH_3I$  was not a major precursor of reactive iodine during the cruise. Significant negative correlation was found between IO and oceanic  $CH_3I$  ( $r = -0.42$ ) and  $CH_2ICl$  ( $r = -0.50$ ), suggesting that a biological mechanism inhibits production or release of iodine from the ocean, in agreement with previous work (Gómez Martín *et al.*, 2013).

A steady-state analysis of IO was conducted, using the measurements of  $I_2$ , HOI + ICl,  $CH_3I$ ,  $O_3$ , and  $NO_2$  made during the cruise, and estimated concentrations of OH,  $HO_2$ , and NO from measurements in the open ocean marine boundary layer reported in the literature. No heterogeneous reactions were included, so the analysis represents a first look at important production and loss processes, and a more detailed modelling study is required to examine the processes in more detail. Photolysis of  $I_2$  was found to be the largest source of IO, with a smaller but significant contribution from photolysis of HOI. The reaction of IO with NO was found to be an important reactive iodine recycling mechanism.

Iodine was not found to play a significant role in tropospheric ozone destruction during the cruise.

Reasonable agreement was found between simultaneous measurements of IO by LIF and MAX-DOAS during cruise SO218, with the mean MAX-DOAS measurement being 0.74 pptv. Similar average daytime profiles of IO were measured by both instruments, with little variation in IO throughout the day. Slightly higher mixing ratios were measured by the LIF instrument, in accordance with the predicted vertical profile of IO above the sea surface (Mahajan *et al.*, 2010, Großmann *et al.*, 2013). Maximum IO columns of  $3 \times 10^{12}$  molecule  $cm^{-2}$  have been measured over the Western Pacific by the SCIAMACHY instrument onboard the Envisat satellite (Schönhardt *et al.*, 2008). Assuming an air mass factor of 1 and a boundary layer height of 1 km, following the work of Gómez Martín *et al.* (2013), this satellite-based measurement corresponds to a mixing ratio of 1.4 pptv. Given the large uncertainty in the satellite measurements (Schönhardt *et al.*, 2008), and the potential influence of IO in the free troposphere on the observed IO column (Dix *et al.*, 2013), there is no clear discrepancy between the satellite measurements and the *in situ* LIF measurements made during the cruise.

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## REPORT 10D: MEASUREMENTS OF I<sub>2</sub> AND THE SUM OF HOI + ICL DURING SHIVA

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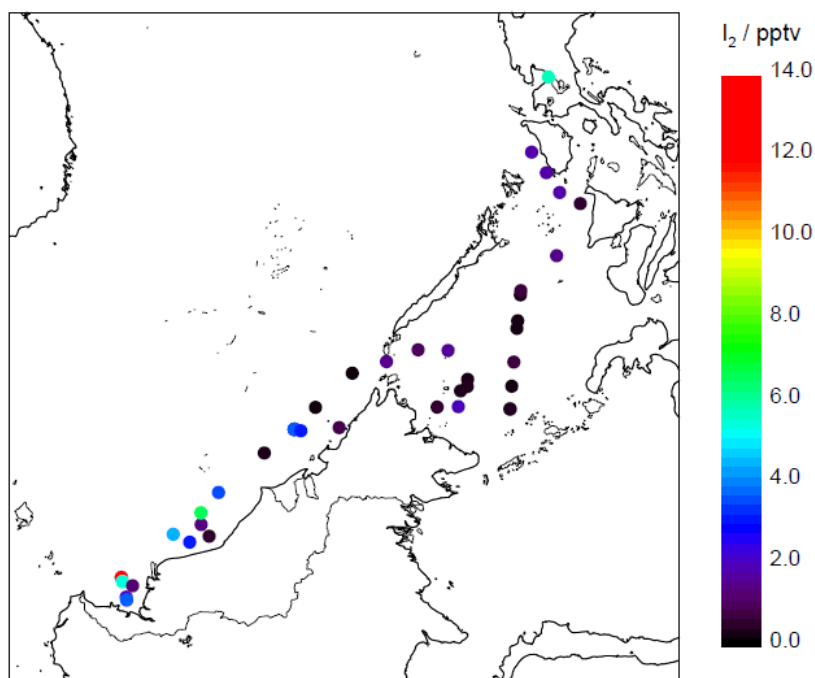
University of Mainz

Measurements of I<sub>2</sub> and the sum of HOI + ICl (collectively termed activated iodine compounds, or AIC) were made using the Denuder Diffusion technique (Huang and Hoffmann, 2009, Huang *et al.*, 2010). Samples were collected by drawing air through glass tubes, coated on the inside with 1,3,5-trimethoxybenzene (1,3,5-TMB) for collection of ICl and HOI, and  $\alpha$ -cyclodextrin/<sup>129</sup>I for collection of I<sub>2</sub>. The tubes were positioned on the port side of the front deck of the RV *Sonne* to minimise the influence of the ship on the sampled air. For each sample, air was drawn through the tubes for 30 minutes by a small diaphragm pump housed in the 10 ft shipping container on the front deck. The tubes were connected to the pump by Teflon tubing. Following sampling, the tubes were sealed and were stored in a freezer. The samples were analysed by Dr Ru-Jin Huang at the University of Mainz, using the gas chromatography/mass spectrometry technique described by Huang and Hoffmann (2009). 47 samples were taken in total.

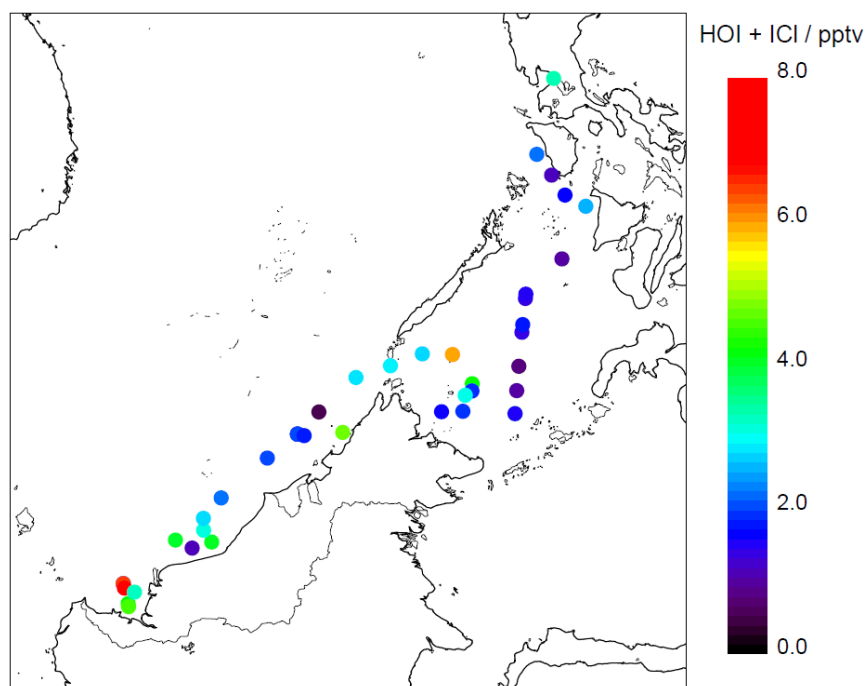
Both I<sub>2</sub> and AIC remained above the detection limit (0.17 pptv) for most of the cruise. The mean I<sub>2</sub> mixing ratio was 1.98 pptv, and the maximum I<sub>2</sub> mixing ratio was 12.74 pptv, measured at night (22:00 local time) during the diurnal station near Kuching. Few measurements of I<sub>2</sub> in open ocean regions are reported in the literature. The I<sub>2</sub> mixing ratios measured during cruise SO218 are generally higher than the 1.5 pptv reported by Finley and Saltzman (2008) in oceanic air on the Californian

coast, and lower than the 10–50 pptv reported by Harris *et al.* (2011) between Singapore and Wellington, New Zealand. The mean AIC mixing ratio was 2.74 pptv, and the maximum AIC mixing ratio was 7.56 pptv, also measured at 07:00 (local time) during the diurnal station near Kuching. No measurements of HOI and ICl over the ocean have previously been reported. Figure 1 and Figure 2 show the SO218 cruise track coloured by the mixing ratios of  $I_2$  and AIC, respectively.

Previous modelling studies of IO have relied upon fluxes of  $I_2$  from the ocean surface to reproduce observations (Furneaux *et al.*, 2010, Großmann *et al.*, 2013). A recent laboratory and modelling study found that HOI, produced in the heterogeneous reaction of  $O_3$  with dissolved iodide at the sea surface, is the dominant inorganic iodine species emitted from the ocean, and is likely to be an important precursor of IO (Carpenter *et al.*, 2013). The measurements of  $I_2$  and AIC made during the SHIVA cruise were therefore a useful tool in predicting the daytime IO concentrations using a steady-state analysis.



**Figure 1.** SO218 cruise track coloured by mixing ratio of  $I_2$ , with low mixing ratios in blue colours and high mixing ratios in red colours.



**Figure 2.** SO218 cruise track coloured by mixing ratio of HOI + ICl (AIC), with low mixing ratios in blue colours and high mixing ratios in red colours.

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## REPORT 11: AEROSOL CHEMISTRY OF HALOGENS DURING SHIVA

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### Introduction

Aerosols play a key role in halogen cycling in the marine atmosphere, with chlorine (Cl) being transferred to the gas phase by acid displacement reactions, bromine (Br) release being induced by reaction of ozone on seasalt particles and iodine (I) chemistry promoting transfer of Cl, Br and I to the gas phase via halogen activation reactions. Ultimately aerosols appear to be net sources for Cl and supermicron Br and net sinks for I and submicron Br.

Although these processes are intimately linked to ozone chemistry, the processes that lead to submicron Br enrichment and those that control aerosol iodine chemistry are very poorly understood at present. In the case of iodine, which has extremely rich and complex aerosol chemistry, there is a severe lack of field data available, with only one published study in the western Pacific region (Lai et al., 2008). The species of iodine commonly found in marine aerosol include iodide ( $I^-$ ), iodate ( $IO_3^-$ ) and a soluble organic iodine (SOI) fraction whose components have yet to be identified (Baker, 2005; Saiz-Lopez et al., 2012). The mechanisms responsible for interchanges between these species, and the overall impact of these interchanges on tropospheric ozone chemistry, are currently unclear.

### Sampling and Analysis

During the SO218 cruise aboard RV *Sonne* 13 aerosol samples were collected for determination of  $Cl^-$ ,  $Br^-$  and iodine speciation, as well as a number of other aerosol ionic components. Each sample was collected for ~24 hours onto pre-cleaned 20 x 25 cm glass fibre filters, using a Tisch total suspended particulate sampler operating at a flow rate of  $\sim 1 \text{ m}^3 \text{ min}^{-1}$ . Aerosol filters were stored frozen until analysis at the University of East Anglia, when soluble components were extracted into ultra-pure water using mechanical shaking at room temperature. Most analytes (including  $Cl^-$  and  $Br^-$ ) were determined by ion chromatography (IC), while iodine analysis was done using both inductively coupled plasma mass spectrometry (ICP-MS) for total soluble iodine (TSI) and IC-ICP-MS for  $I^-$  and  $IO_3^-$ . Soluble organic iodine (SOI) concentrations were then determined as the difference between TSI and the sum of  $I^-$  and  $IO_3^-$ .

### Results

Overall chemistry of the aerosol samples collected during the SHIVA campaign is consistent with the composition of other marine-dominated environments. Here we focus on the results obtained for bromide and the iodine species.

In Figure 1 we show enrichment factors (EF) relative to seawater composition (Eqn 1) for both  $Br^-$  and iodine (TSI). EF values greater than 1 indicate that the element concerned is enriched relative to seawater composition, while values less than 1 indicate that the element is depleted.

Eqn 1. 
$$EF_X = \frac{[X]_{aero}}{[X]_{sw}}$$
, where X is Br or I and the subscripts *aero* and *sw* refer to the aerosol sample and seawater respectively.

For bromide, all samples were depleted. This indicates that aerosols are a net source of bromine to the atmosphere in this region, and that depletion processes in super-micron aerosol particles probably outweigh enrichment in sub-micron particles (Sander et al., 2003). For iodine, the opposite behaviour



was observed, with all samples being enriched (to factors of 35-320 above seawater composition). This behaviour has been observed in several other marine (and terrestrial) environments (Baker et al., 2000; Duce et al., 1967) and indicates that aerosol is a net sink for iodine emitted from the sea surface.

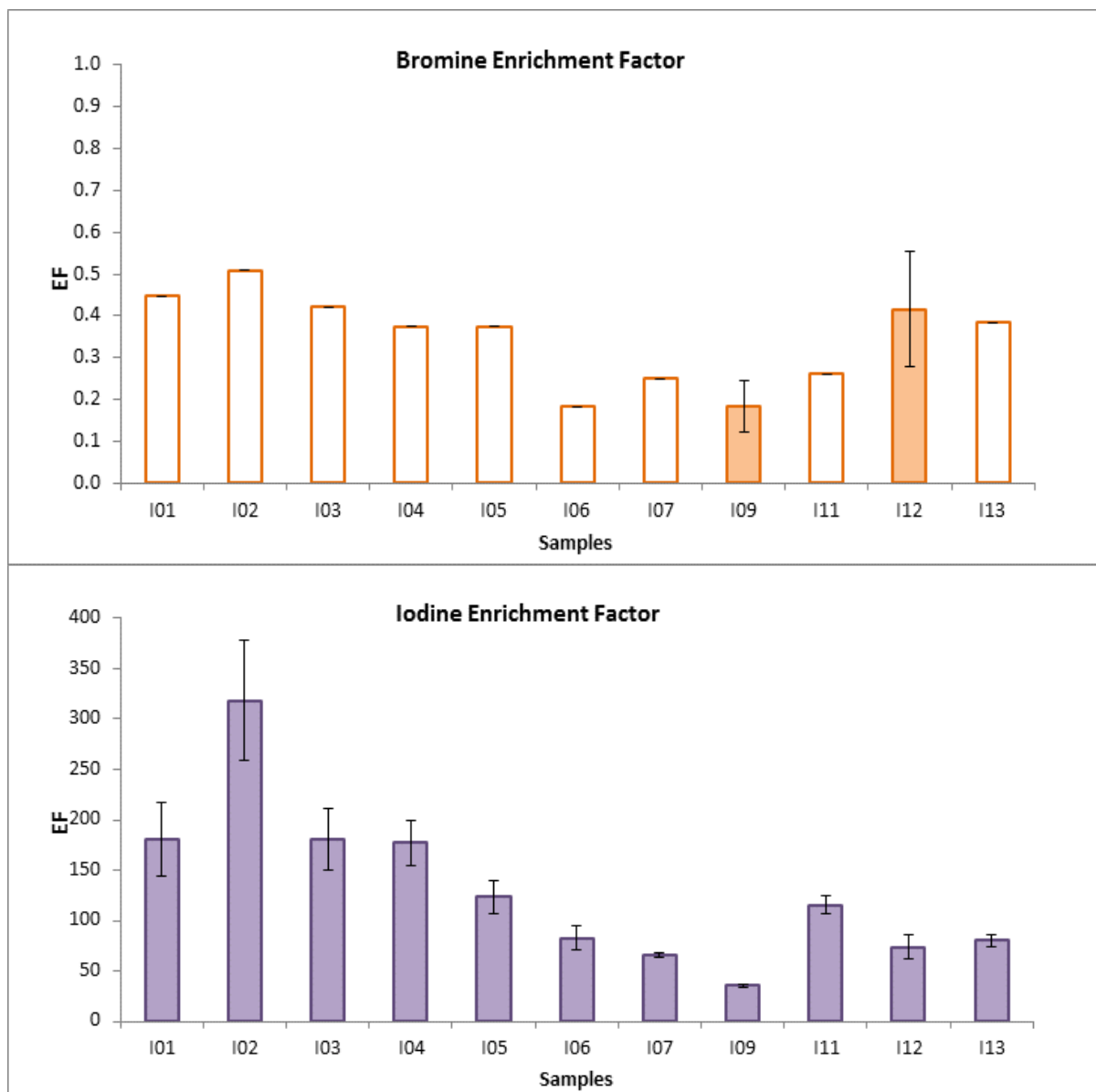


Figure 1. Enrichment factors (relative to seawater composition) for bromide and total soluble iodine. Note that unfilled bars in upper panel indicate samples for which bromide concentrations were below analytical detection limits. These bars therefore show the possible range of EF values for these samples.

In Figure 2 we show the speciation distribution of iodine between iodide, iodate and SOI in the SHIVA aerosol samples. This illustrates that all three species make significant contributions to the aerosol contribution in the region, although there is considerable sample-to-sample variability in the relative proportions of each species. Relative to samples collected from other environments, the SHIVA samples generally contain rather higher proportions of iodide and lower proportions of iodate than, for example, aerosols containing Saharan dust (Allan et al., 2009; Baker, 2005; Yodle,

unpublished data). We are continuing our efforts to understand the factors that control aerosol halogen chemistry and its impact on tropospheric ozone chemistry.

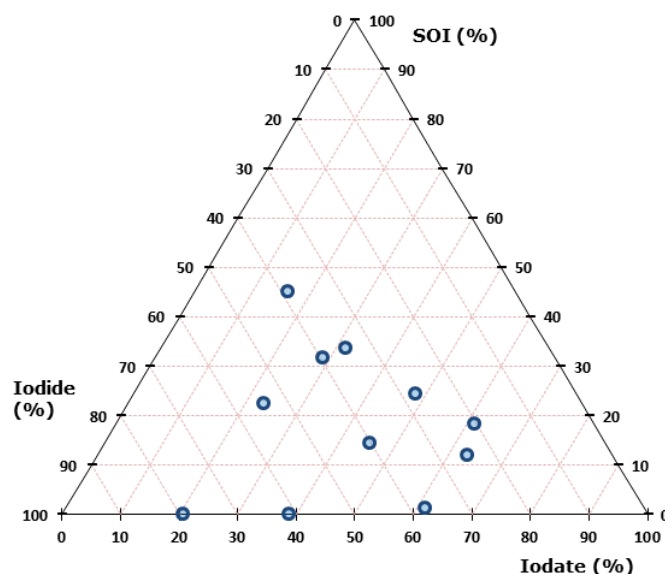


Figure 2. Ternary composition diagram for iodine species in SHIVA aerosol samples. Each axis shows the percentage of iodide, iodate and soluble organic iodine (SOI) contained in each aerosol sample.

## References

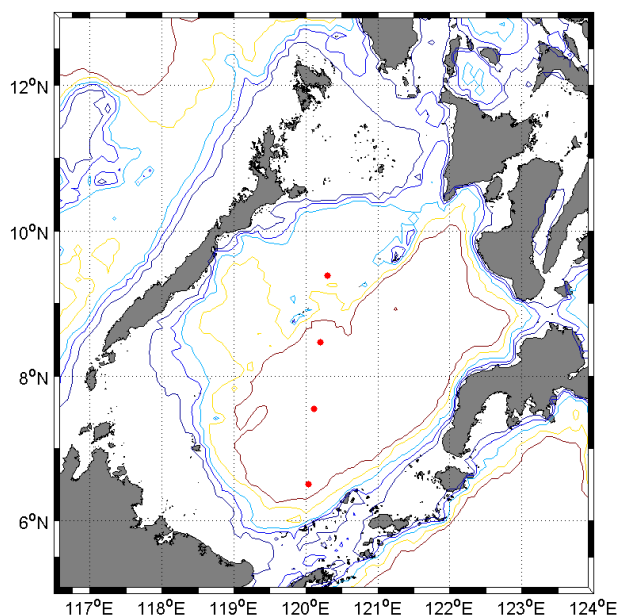
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## REPORT 12: OCEANIC CIRCULATION -TRANSIENT TRACER MEASUREMENTS DURING CRUISE SONNE-218

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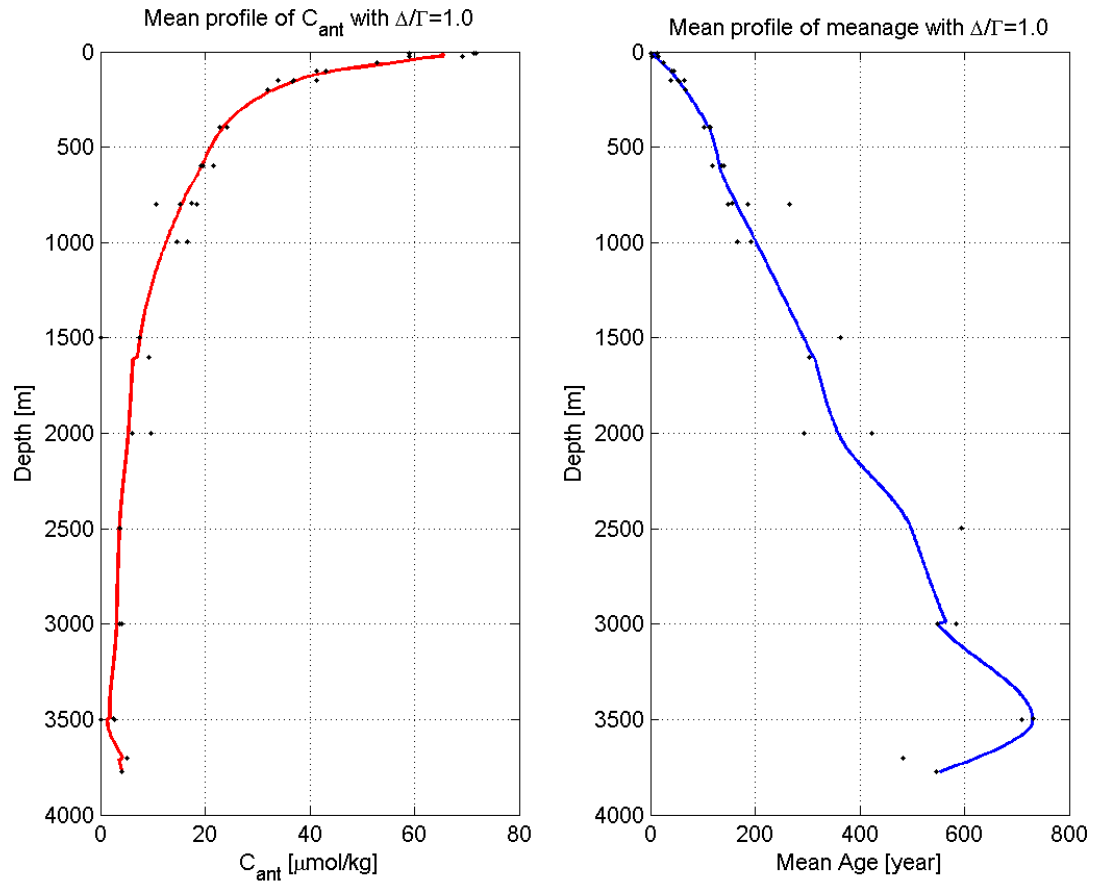
Samples for the measurements of CFC-12 and SF<sub>6</sub> were collected at 4 stations in the central Sulu Sea, Figure 1. The samples were the first to be taken from the Rosetta, were taken in 300 ml glass ampoules and were flame sealed in the lab immediately after sampling, leaving a small head-space of pure N<sub>2</sub> over the water sample. The samples were measured in the lab in Kiel during 2012 using a technique that also measures the tracer content in the head-space of the ampoules.



**Figure 1:** Stations that were sampled for CFC-12 and SF<sub>6</sub> measurements. These are stations 28, 29, 32 and 35.

### Preliminary results:

The CFC-12 profiles from the 4 stations are very similar to each other, indicating small horizontal variability of ventilation within the Sulu Sea. We therefore present a figure of the average profile of anthropogenic carbon and mean ages in the Sulu Sea, Figure 2. These two properties were calculated with the measured CFC-12 data, applying the transit time distribution (TTD) method. Comparison of the CFC-12 and SF<sub>6</sub> data suggest that an inverse Gaussian distribution (IG) of the TTD with the two parameters  $\Delta$  (i.e. the “width” of the IG-TTD) and  $\Gamma$  (i.e. the mean of the TTD) set equal (i.e.  $\Delta/\Gamma=1$ ) well represent the data. The profile of the anthropogenic carbon in the Sulu Sea show relatively high concentrations at the surface, which is expected due to the high temperatures, and rapidly declining concentration with depth. The mean age (i.e. the  $\Gamma$  of the IG-TTD) shows rapidly increasing ages towards depth, reaching about 600 years in the bottom waters, although ages over 400 years are very uncertain due to analytical difficulties in measuring CFC-12 at such low concentrations. This suggests that the Sulu Sea is slowly ventilated and implies a small inventory of anthropogenic carbon ( $C_{\text{ant}}$ ).



**Figure 2:** Mean profiles of the anthropogenic carbon content (left panel) and the mean age (right panel) of the Sulu Sea. These values are calculated using CFC-12 data and the TTD method.

# REPORT 13A: RESULTS OF THE LOCAL BOAT DEPLOYMENTS IN KUCHING, KOTA KINA BALU, AND SEMPORNA

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The South China Sea is a marginal sea of the western Pacific Ocean, encompassing an area from the Singapore and Malacca Straits to the Strait of Taiwan. The Celebes Sea is connected to the South China Sea through the Sulu Sea. In conjunction with European and Malaysian research partners, the SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) Western Pacific field campaign was performed in the fall of 2011. The core field campaign took place in the South China Sea and along the coastline of Peninsula Malaysia and Borneo using the German Research Vessel (RV) Sonne during a cruise leading from Singapore to Manila, Philippines (Figure 1)

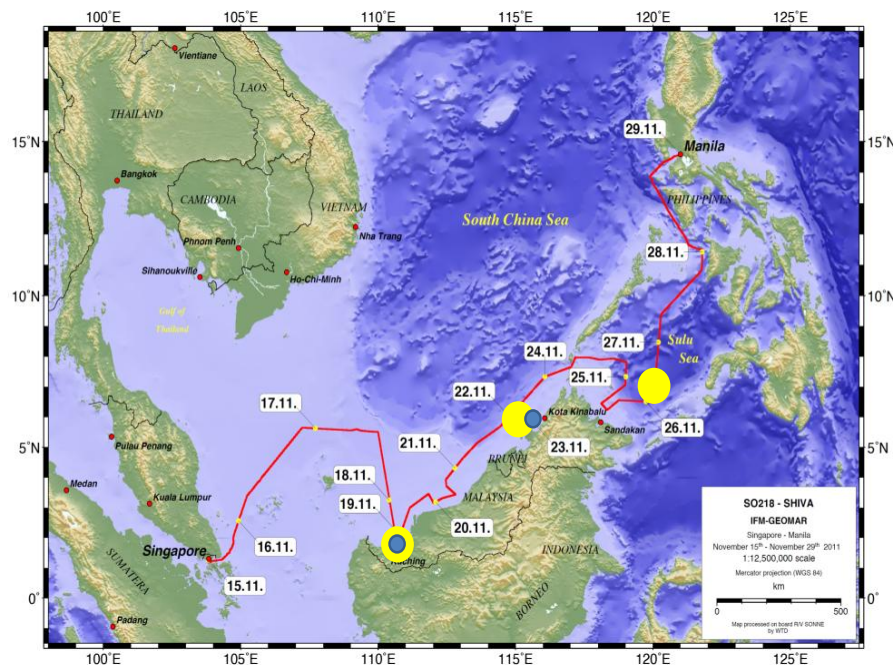


Figure 1: Cruise track of *RV Sonne*: Singapore-Manila (15-29 November 2011), including the local boat meetings at Kuching and Kota Kinabalu (blue circles) and overflights by the DLR air craft Falcon (yellow circles).

Local cruises took place in Kuching on both November 16 and 19, 2011 (see Figure 2 for sampling stations), Kota Kinabalu (November 23, 2011; see Figure 3 for sampling stations) and Semporna (November 26, 2011; see Figure 4 for sampling stations) to provide additional data from near shore locations and coastal influence.

Table 1: Locations of sampling stations at Kuching, Kota Kinabalu and Semporna.

Sampling stations	GPS coordinates			
	Kuching (1611)	Kuching (1911)	Kota Kinabalu	Semporna
Station 1	1°38'36.24"N, 110°30'5.28"E	1°39'28.81"N, 110°31'24.42"E	6° 3'4.56"N, 116° 5'54.60"E	4°35'15.96"N, 118°32'58.14"E
Station 2	1°39'44.82"N, 110°32'7.26"E	1°42'44.24"N, 110°33'23.46"E	6° 3'5.82"N, 116° 4'1.45"E	4°38'37.86"N, 118°20'25.44"E
Station 3	1°42'2.80"N, 110°37'12.36"E	1°45'32.93"N, 110°35'16.86"E	6° 3'4.02"N, 116° 0'2.77"E	4°42'31.68"N, 118°23'19.38"E
Station 4	1°42'46.62"N, 110°39'17.40"E	1°48'2.16"N, 110°37'51.53"E	6° 2'49.85"N, 115°57'38.26"E	4°40'42.48"N, 118°32'11.34"E
Station 5	1°45'49.07"N, 110°41'27.77"E	1°50'54.15"N, 110°40'11.26"E	6° 4'23.64"N, 115°54'36.42"E	4°37'31.26"N, 118°41'5.99"E
Station 6	N/A	N/A	N/A	4°35'56.76"N, 118°43'19.14"E
Station 7	N/A	N/A	N/A	4°35'30.66"N, 118°42'17.10"E
Station 8	N/A	N/A	N/A	4°33'17.83"N, 118°39'22.57"E

\*1611 and 1911 denotes November 16 and 19, 2011 respectively.

\*\*N/A denotes coordinates are unavailable.

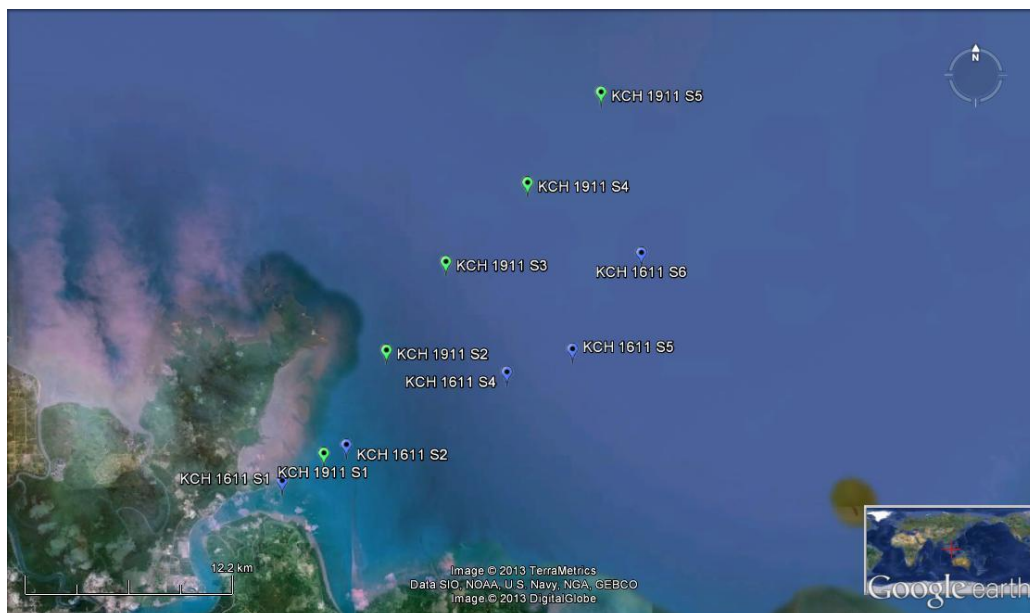


Figure 2: Locations of sampling stations in Kuching, Sarawak.





Figure 3: Locations of sampling stations in Kota Kinabalu, Sabah.

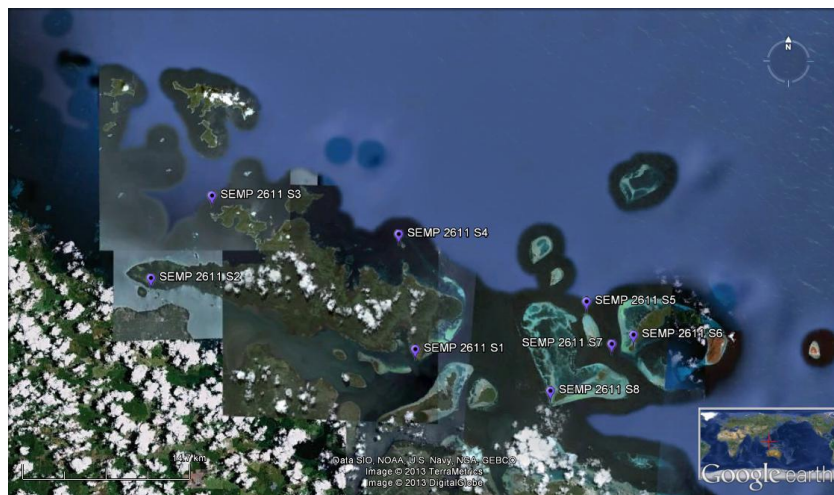


Figure 4: Locations of sampling stations in Semporna, Sabah.

### Physico-chemical parameters

Basic physico-chemical parameters were recorded during sampling in Kuching (November 19, 2011) and Kota Kinabalu (see Table.2). Values for Semporna are not reported as the measuring instruments were inconsistent and not functioning properly at the time of sampling.

Table 2: Physico-chemical parameters measured from Kuching and Kota Kinabalu.

Station	Depth (m)	Temperature (°C)	pH	Salinity (ppt)	Nitrate (ppm)	Phosphate (ppm)	Nitrite (ppm)	Silicate (ppm)
KCH-1	1	29.06	7.90	28.48	9.13	0.60	1.46	23.47
	5	29.34	8.10	30.59	ND	ND	ND	ND
KCH-2	1	28.98	8.25	30.65	2.02	0.33	0.60	7.48
	5	29.11	8.25	30.89	ND	ND	ND	ND
KCH-3	1	29.05	8.33	31.18	0.85	0.15	0.03	2.97
	5	29.16	8.30	30.53	ND	ND	ND	ND
KCH-4	1	29.00	8.33	31.07	0.49	0.10	0.00	4.52
	5	29.10	8.29	30.52	ND	ND	ND	ND
KCH-5	1	29.27	8.31	31.61	0.15	0.06	0.00	5.86
	5	29.40	8.29	31.85	0.15	0.05	0.00	2.21
<b>KCH</b>		<b>29.15</b>	<b>8.24</b>	<b>30.74</b>	<b>2.13</b>	<b>0.22</b>	<b>0.35</b>	<b>7.75</b>



<b>mean</b>								
KK-1	1	29.80	8.44	31.85	1.04	0.15	ND	3.47
	5	29.90	8.37	32.04	ND	ND	ND	ND
KK-2	1	29.73	8.36	31.44	0.25	0.17	ND	3.21
	5	29.78	8.33	31.95	ND	ND	ND	ND
KK-3	1	29.55	8.34	31.88	0.23	0.11	ND	2.67
	5	29.54	8.33	31.87	ND	ND	ND	ND
KK-4	1	29.52	8.36	31.93	ND	ND	ND	ND
	5	29.45	8.34	31.91	ND	ND	ND	ND
KK-5	1	29.68	8.38	32.03	0.13	0.03	ND	2.74
	5	29.50	8.37	31.92	0.15	0.02	ND	2.79
<b>KK mean</b>		<b>29.65</b>	<b>8.36</b>	<b>31.88</b>	<b>0.36</b>	<b>0.10</b>	<b>ND</b>	<b>2.98</b>

\*KCH denotes Kuching; KK denotes Kota Kinabalu.

\*\*ND denotes values are not detectable.

Sampling stations at Kota Kinabalu stretched further away from the coastline and displayed average values of salinity at 31.88 ppt, pH of 8.36 and temperature of 29.65 °C (see Table 3.2). The first sampling station at Kuching (KCH-1) was closer to the river mouth of the Sarawak river and displayed a visible influence by riverine water with its surface water displaying a salinity of 28.48 ppt and pH of 7.90 (see Table 2). The salt and minerals in sea water made it denser than fresh water thus at the mouth of the river where it meets the sea, the fresh water flows downstream across the surface and the sea flows upstream at the bottom, resulting in an increasing trend from low to high salinity as it goes deeper (salinity at depth is 2 units higher; Table 2). The pH values at KCH-1 also showed an increase from pH 7.90 at 1 m depth to pH 8.10 at 5 m depth.. Subsequent stations were however more representative of ocean waters with pH around 8.3 and salinity around 31ppt (Table 3.2). Temperatures at Kuching and Kota Kinabalu are consistent at both 1 and 5 m depth (mean temperature of 29.15 and 29.65 °C respectively; see Table 2).

The riverine input at Kuching was also visible with significantly higher nitrate, phosphate, nitrite, and silicate values closer to the river mouth (KCH-1 and KCH-2; see Table 2). Nutrient levels in Kuching were also generally higher than in Kota Kinabalu. To assess differences in distribution in the upper surface layers, samples were also taken from 5 m depth (KCH-5 and KK-5; see Table 2). Interestingly, the samples for Kota Kinabalu show 'identical' values, however, for Kuching, the silicate drops from 5.86 ppm to 2.21 ppm within the first 5 metres (Table 2).

### REPORT 13 B: RESULTS OF THE LOCAL BOAT DEPLOYMENT KUCHING

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As part of complementary three-part series of local boat deployments, two transects were organised in Kuching on the 16<sup>th</sup> and 19<sup>th</sup> November 2011 respectively. Air and water samples were collected at 5 stations with intervals of 5 km, along transects at 1 to 20 km off the Kuching coasts (see Figure 1 below).

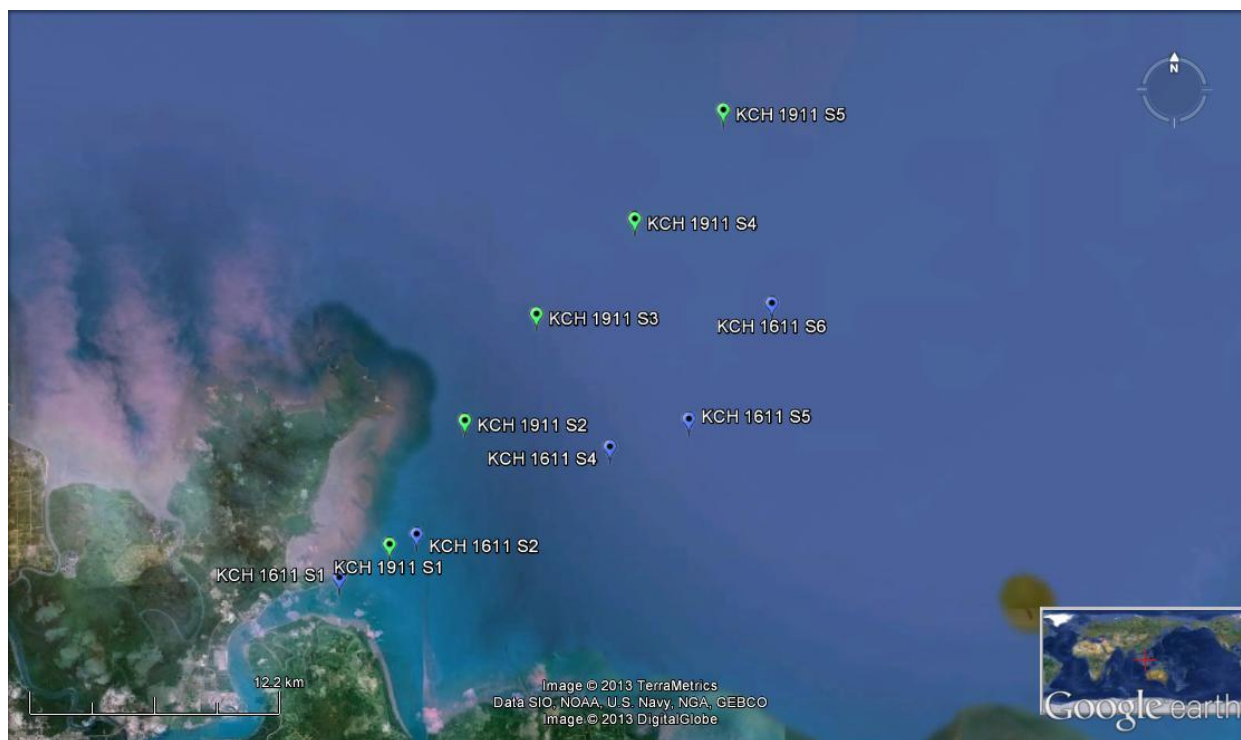


Figure 1: Locations of sampling stations in Kuching, Sarawak.

The main aims of the local boat deployments were two-fold: (i) to obtain coastal samples to complement open ocean samples made by RV Sonne, Falcon aircraft and satellites; (ii) to enable the exchange of samples collected at the coasts (e.g. VSLs and nutrients) to be taken onboard RV Sonne for further analyses, and those collected onboard RV Sonne (sensitive biological samples) to be taken back to UNIMAS and Swinburne labs for storage and further analyses. The rendezvous station was at the RV Sonne diurnal station on the 19<sup>th</sup> November 2011. Measured parameters include VSLs in seawater and air (UEA, UM), plankton biological sampling (UNIMAS, UMS), and selected surface and subsurface water parameters (UNIMAS, SUTS). Also collected were samples for baseline

information on bacterial communities in Kuching (SUTS), for further comparisons to bacterial communities at other local boat deployment sites (Kota Kinabalu, Semporna), and with regards to *in situ* physico-chemical parameters. The first sampling station at Kuching was close to the river mouth of the Sarawak river and displayed a visible influence by riverine water with its surface water displaying a salinity of 28.48 ppt and pH of 7.90 (data not shown). The riverine input at Kuching was also visible with significantly higher nitrate, phosphate, nitrite, and silicate values closer to the river mouth (data not shown). Nutrient levels in Kuching were also generally higher than in Kota Kinabalu. To assess differences in distribution in the upper surface layers, samples were also taken from 5 m depth (data not shown). Interestingly, the samples for Kota Kinabalu show 'identical' values, however, for Kuching, the silicate drops from 5.86 ppm to 2.21 ppm within the first 5 metres (data not shown), indicative of an active biological pump. From Kuching waters, 89 bacterial isolates were obtained over the two sampling periods (November 16 and 19, 2011). The total bacterial assemblage had representatives within the *Alpha*-, *Beta*- and *Gammaproteobacteria*, as well as *Firmicutes*, however, the diversity and distribution were depth dependent. Bacteria isolated from Kuching displayed the highest abundance of both DMSP degrading genes (36%) compared to communities isolated from Kota Kinabalu and Semporna with 13 and 19 %, respectively. Our findings indicate that the community structure of *Gammaproteobacteria* in the area could be tightly linked to the local sulphur and also possibly the nitrogen cycle. The community structure of *Pseudo-nitzschia* species was also identified based on genetic information by using the automated ribosomal intergenic spacer analysis (ARISA). Amplification was carried out on a total of 75 surface water samples (collected during local and SHIVA cruise), and the amplicons were analyzed by fragment analysis using DNA analyzer. Total of 50 ribotypes were detected. Community structure of *Pseudo-nitzschia* along the eastern SCS was characterized. Clustering analysis revealed a degree of community structuring in *Pseudo-nitzschia*. The results showed two linkages, one cluster with locations being dominated by *P. caciantha* ribotype 2; and the other with locations where *P. caciantha* is absent. However, no significant variation was found between samples collected from coastal water or Open Ocean.

**REPORT 13 C: RESULTS OF THE LOCAL BOAT DEPLOYMENT KOTA KINABALU,**

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During the Kota Kinabalu (KK) local ship cruise on 23 November 2011, selected water parameters (light, temperature, salinity, pH, demand oxygen (DO)) were measured at 5 sampling stations to support the SHIVA program.

The range of temperature ( $^{\circ}\text{C}$ ), pH, salinity (psu), DO (mg/L) during this sampling was  $29.49 \pm 0.14^{\circ}\text{C}$ ,  $8.33 \pm 0.02$ ,  $32.09 \pm 0.05$  psu,  $3.44 \pm 0.16$  mg/L, respectively. Salinity at water surface was increasing while temperature, DO, pH and light were decreasing with water depth. Horizontal and vertical fluctuation of the parameters were mainly due to change of weather condition. For example, light value at water surface were slightly low at St1 where field measurement was conducted around 5:50am and increased at St 4 (-11 am) where sky is clear from cloud cover. Higher water temperature and salinity at St 5 when sampling were conducted near noon time and far away from mainland, respectively.

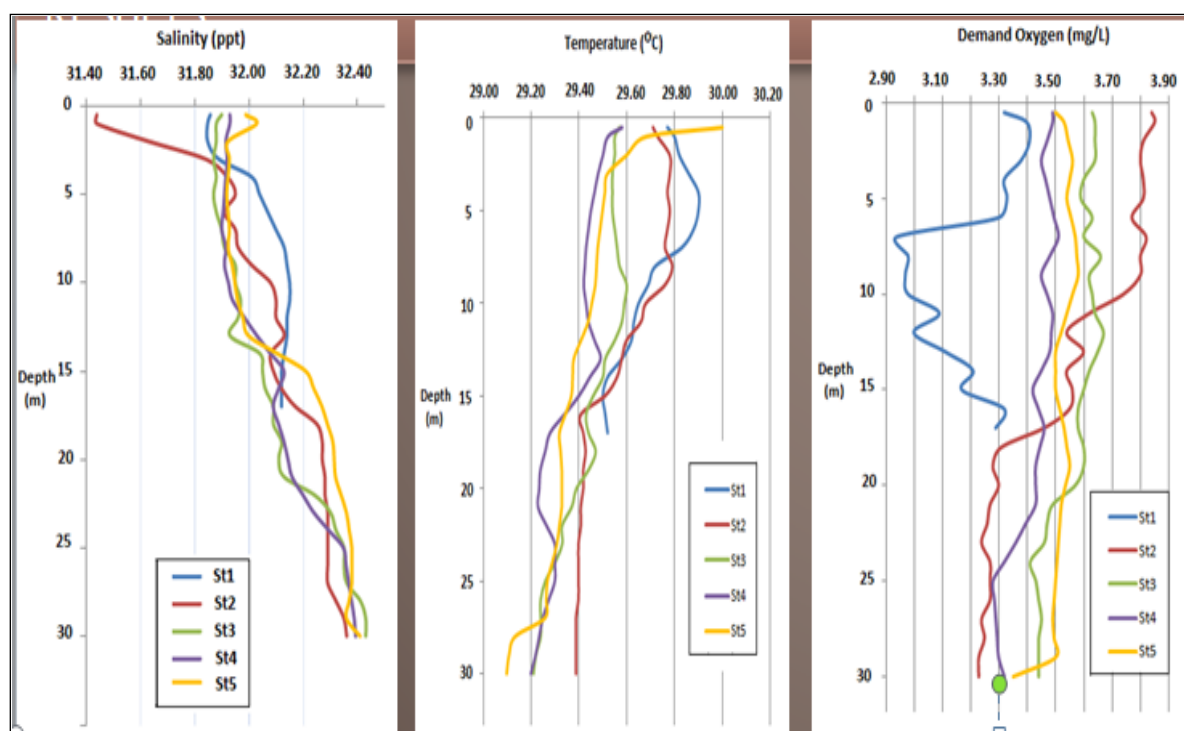


Figure 1: Physico-chemical parameters (salinity, temperature, oxygen demand) at the five stations off the coast of Sabah during the local ship cruise at Kota Kinabalu on 23<sup>rd</sup> November 2011.

The local boat cruise in KK characterized the microbial, phytoplankton and zooplankton communities which are potential biogenic sources of halogenated compounds.

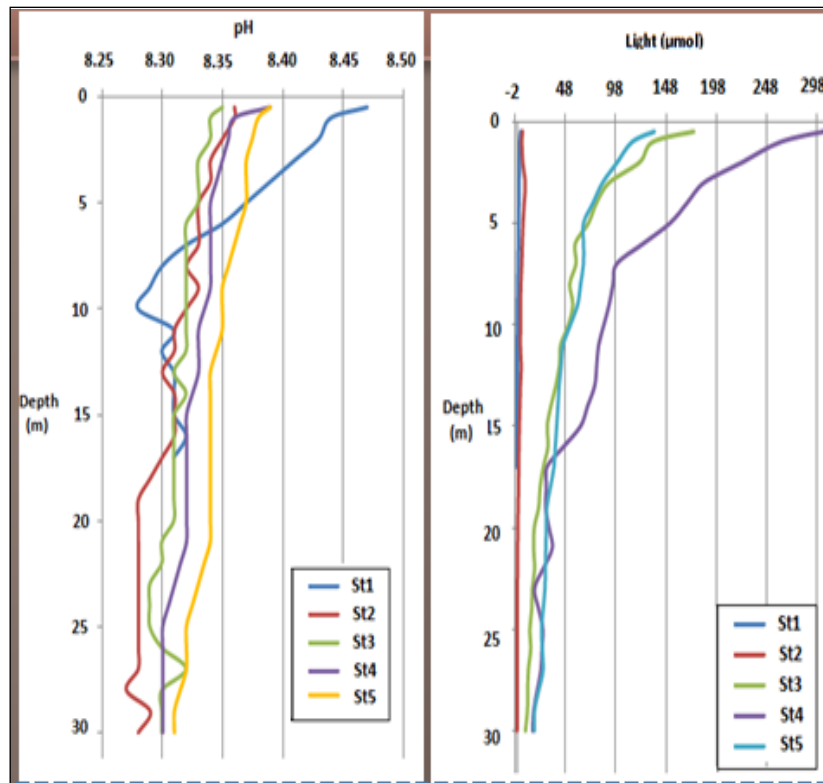


Figure 2: Physico-chemical parameters (pH, Light) at the five stations off the coast of Sabah during the local ship cruise at Kota Kinabalu on 23<sup>rd</sup> November 2011.

In particular the cruise was conducted in an region infested with harmful algal blooms of the high-growth biomass microalgae *Cochlodium polykrikoides* (Figure 3).



Figure 3 : Harmful microalgae blooms of *C. polykrikoides* in KK coastal waters

Results showed a high diversity and abundance of species in the coastal areas (stations 1-2) compared to the offshore stations (3-5)

This can be related to similar trends in bromoform concentrations which decreased from 100pmol/L at station 1 to 30 pmol/L at station 5 (Shi , 2013, Report 1a).

Phytoplankton species identification and fluorometer measurements during the coastal cruise can be used to calibrate against the satellite imagery data for chlorophyll a.

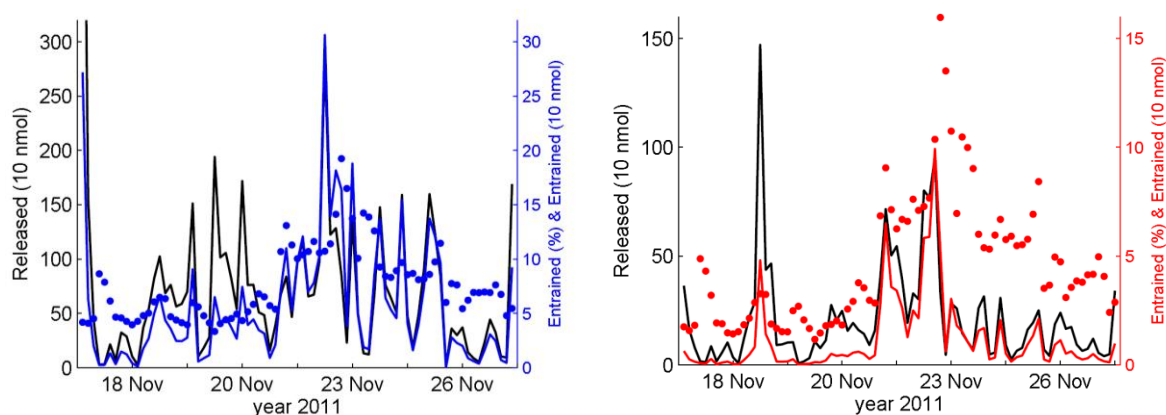
## REPORT 14: THE CONTRIBUTION OF OCEANIC HALOCARBONS TO THE STRATOSPHERIC HALOGEN LOADING

Susann Tegtmeier, Kirstin Krüger, Birgit Quack

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We investigate the contribution of oceanic halocarbons to the stratospheric halogen budget. Based on  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$  measurements during the SHIVA ship campaign and Lagrangian transport calculations we provide a detailed analysis of halocarbon transport from the ocean surface to the cold point in the upper tropical tropopause layer (TTL). The level above which no significant washout is expected is particularly important for stratospheric halogen chemistry, since all  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$  which reaches this level before being chemically destroyed can be expected to contribute to the stratospheric halogen budget. While the exact altitude of the ‘no-washout level’ is still under debate we have chosen the cold point altitude at approximately 17 km as an upper estimate since no dehydration is expected to occur above.

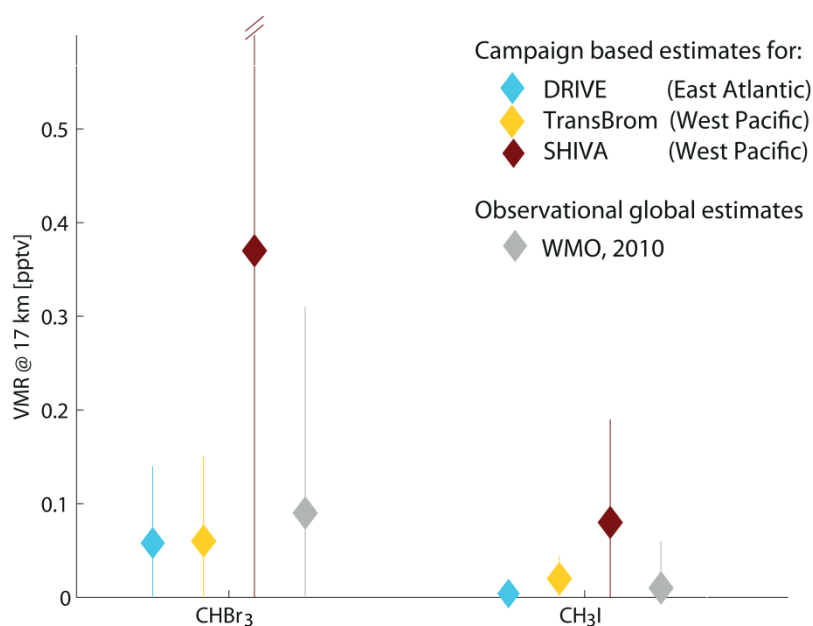
The atmospheric transport of  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$  from the oceanic surface into the upper troposphere and TTL is simulated with the Lagrangian particle dispersion model FLEXPART. This model includes parameterizations for moist convection, turbulence in the boundary layer and free troposphere, dry deposition and in-cloud as well as below-cloud scavenging, and the simulation of chemical decay. In order to describe the transport, dispersion and convection of  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$ , we simulate trajectories of a multitude of air parcels. For each data point of the observed sea-to-air flux a separate FLEXPART run is launched where 10000 air parcels were released over one hour from a  $0.0002^\circ \times 0.0002^\circ$  grid box ( $\sim 500 \text{ m}^2$ ) at the ocean surface centered at the measurement location. The total amount of  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$  emitted from this grid box over one hour is calculated based on the observation-derived flux and uniformly distributed over the 10000 air parcels. The FLEXPART runs are driven by the 6-hourly fields of horizontal and vertical wind, temperature, specific humidity, and precipitation from the ECMWF reanalysis product ERA-Interim. Trajectories were terminated after 3 months for  $\text{CHBr}_3$  and after 7 days for  $\text{CH}_3\text{I}$  according to their atmospheric life times.



**Figure1.** Emissions (black line), as well as the relative (colored dots) and total (colored line) amount of  $\text{CHBr}_3$  (left panel) and  $\text{CH}_3\text{I}$  (right panel) entrained above 17 km are displayed as a function of time along the cruise track. Emissions are calculated from the observed flux for a time period of one hour and an area of  $500 \text{ m}^2$  for each observation.

Figure 1 shows the oceanic emission rates (black lines) of  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$  as observed during the SHIVA ship campaign. The emission strength along the cruise track demonstrates the large variability of air–sea fluxes during the campaign with the measurement locations often about less than 100 km apart from each other. The contribution of  $\text{CHBr}_3$  ( $\text{CH}_3\text{I}$ ) to the stratospheric halogen loading is based on the amount of the gas entrained above 17 km, calculated as the sum of  $\text{CHBr}_3$  ( $\text{CH}_3\text{I}$ ) carried by all the computational particles across this altitude. For  $\text{CHBr}_3$ , about 5-10% of the emitted gas is entrained above 17 km during most of the cruise. Stronger vertical transport with 10-15% entrainment is taking place during 22-23 November 2011. Atmospheric  $\text{CHBr}_3$  abundance at 17 km averaged over the whole campaign amounts to 0.38 ppt, while maximum abundances of 1.8 ppt are associated with strong vertical transport and large emissions on 22 November. For the much shorter lived  $\text{CH}_3\text{I}$ , only about 2-3% of the oceanic emissions are transported above 17 km. Events of very efficient vertical transport are again predicted for the section 22-23 November 2011. Here, the model estimates 0.6 ppt  $\text{CH}_3\text{I}$  at 17 km which is much larger than any values reported by high reaching aircraft measurements so far. The campaign average mixing ratio at 17 km is somewhat lower amounting to 0.07 ppt.

Compared to other oceanic regions (i.e., the tropical Atlantic) an overall stronger vertical transport is estimated for the SHIVA campaign which took place in the coastal regions of the maritime continent an area well known for deep cumulus convection and heavy precipitation systems during boreal winter. Figure 2 shows the campaign averaged mixing ratios at 17 km estimated for the SHIVA ship campaign as well as for the Sonne TransBrom ship campaign in the open ocean West Pacific in October 2009 and the DRIVE ship campaign in North East Atlantic in May/June 2010. Additionally, global estimates based on measurements of high reaching aircrafts are displayed. For both gases, estimates based on the SHIVA campaign are much larger than estimates based on other campaigns or on aircraft observations demonstrating the importance of the coastal regions of the maritime continent as a source region for stratospheric halogens. For  $\text{CHBr}_3$ , the SHIVA based estimate is about 0.38 ppt while the estimates from the two other campaigns and the aircraft observations range between 0.06 and 0.09 ppt. For  $\text{CH}_3\text{I}$ , the emissions reported during SHIVA result in 0.07 ppt at 17 km, while the other two ship campaigns as well as aircraft observations give 0.01 – 0.02 ppt. Note that the aircraft campaigns are located in the tropical East Pacific and can be expected to differ from West Pacific abundances.



**Figure2.**  $\text{CHBr}_3$  and  $\text{CH}_3\text{I}$  mixing ratios at 17 km estimated for three tropical campaigns and based on aircraft measurements.



For both gases the largest total entrainment takes place on 22-23 November 2011 (Figure 1) and is based on large emissions during times of maximum efficiency of vertical transport. Individual sections of the SHIVA ship campaign cruise with high correlations between emission and vertical transport have been identified. The analysis of the meteorological conditions during the campaign leads to the hypothesis that the horizontal surface winds act as a connecting link between emission and transport. On the one hand, horizontal wind strength directly determines the emission strength by diluting  $\text{CHBr}_3$  or  $\text{CH}_3\text{I}$  rich air and thereby controlling the uptake capacities of the atmosphere. On the other hand, horizontal wind variations depend on the meteorological conditions such as convective systems or storm events. In particular, strong horizontal winds associated with tropical cyclones (i.e., typhoons) can indicate efficient vertical uplift possibly penetrating the stratosphere and thereby complete the line of argument connecting emission strength and troposphere-stratosphere transport.

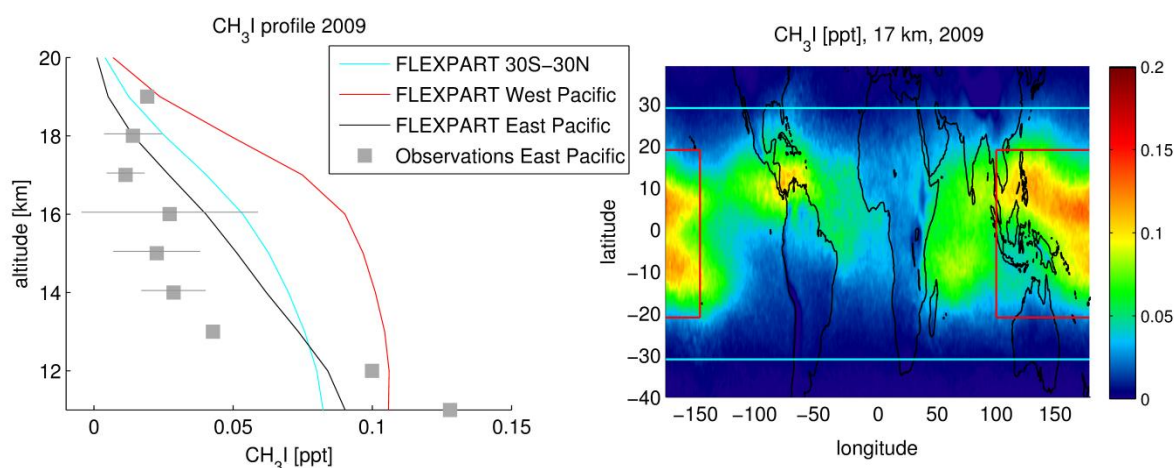
In order to analyze whether the relatively large mixing ratios estimated for the West Pacific emissions are isolated cases strongly deviating from otherwise low  $\text{CH}_3\text{I}$  abundances or if they occur frequently enough to impact global  $\text{CH}_3\text{I}$  in the upper TTL, we analyze global model runs in addition to campaign based estimates. We quantify the global contribution of  $\text{CH}_3\text{I}$  to the stratospheric halogen budget from FLEXPART model runs using a global emission climatology provided by Ziska et al. (2013) as input data. We compare modeled  $\text{CH}_3\text{I}$  abundances to available aircraft measurements in the free troposphere and TTL region. A special focus is on the model-measurement comparison in the upper TTL and on the question whether the here available aircraft measurements are representative of existing global estimates. In a first step coincident data points for observations and model output are identified if they are less than 12 hours apart and if their distance is less than  $0.5^\circ$  horizontally and less than 0.5 km vertically. Profile comparisons are determined for each campaign by taking the mean and standard deviation over all coincidences identified for the particular campaign data and for the corresponding model output.

The profile comparison for three aircraft campaigns, which provide data in the free troposphere and lower UTLS, show in general a good agreement between the observations and the model results with the latter being consistently lower (not shown here). For the SHIVA aircraft campaign, observed and modeled profiles show a very similar shape with FLEXPART results being slightly smaller consistently over the whole altitude range. The largest differences are found around 11 km. For some individual flights convective outflow leads to observations of enhanced  $\text{CH}_3\text{I}$  between 10 and 12 km resulting in a ‘‘C-shape’’ profile a characteristic which is well captured by the model results (not shown here).

Model-measurement comparisons for four campaigns conducted with the high altitude aircraft sampling in the upper TTL and lower stratosphere give an overall good agreement above 10 km. The aircraft campaign based mixing ratios in the upper TTL are below 0.1 ppt with the exception of the strongly enhanced mixing ratios at 16 km during ACCENT over Central America in 1999, which are reported by the observations and the model results. Largest discrepancies are found for the TC4-WB57 campaign over Central America in 2007, where basically no  $\text{CH}_3\text{I}$  was observed above 15 km while FLEXPART simulates mixing ratios around 0.1 ppt for the levels 13-17 km. Only below 10 and above 17 km the model output agrees well with the TC4-WB57 observations.

A summary of the model-measurement comparison in the upper TTL is displayed in Figure 3 where the observed profiles averaged over all four campaigns are displayed (grey squares). Additionally, the modeled  $\text{CH}_3\text{I}$  abundance in the aircraft campaign region is shown (black line). FLEXPART slightly overestimates the amount of  $\text{CH}_3\text{I}$  observed at 17 km (0.01 ppt) simulating a too strong  $\text{CH}_3\text{I}$  entrainment. However, the model results underestimate  $\text{CH}_3\text{I}$  at 19 km which is suggested to be around 0.02 ppt according to observations. The overall comparison of the 17-19 km region gives a good

agreement between observations (0.011-0.019 ppt) and model results (0.006 – 0.032 ppt). It is of interest to estimate  $\text{CH}_3\text{I}$  abundances in regions where no in-situ measurements in the upper TTL are available. The West Pacific region is of particular importance for the troposphere-stratosphere transport, and we will evaluate how the FLEXPART results in this area compare to the model results and observations in the East Pacific. Such a comparison will allow speculations of how representative existing aircraft measurements are of global estimates. Figure 3 shows in addition to the observations and FLEXPART results in the East Pacific, the model estimates averaged over the whole tropical belt ( $30^\circ\text{N}$  -  $30^\circ\text{S}$ ) and the tropical West Pacific. While for the West Pacific and the tropical belt the 2009 annual mean is displayed the East Pacific average is based on the months when aircraft measurements are available in order to allow for a comparison of the model East Pacific mean values with the in-situ observations. The observations and model results for the East Pacific agree quite well, as discussed above for the comparisons based coincidences. While observations suggest 0.01 ppt  $\text{CH}_3\text{I}$  at 17 km the modeled profile shows slightly larger values of 0.02 ppt. Overall, the comparison indicates that the available in-situ measurements provide representative estimates of the mean  $\text{CH}_3\text{I}$  abundance in the East Pacific region. FLEXPART results for the West Pacific region show considerable larger mixing ratios especially between 14 and 18 km with 0.08 ppt  $\text{CH}_3\text{I}$  at 17 km. The geographical distribution of the mixing ratios is displayed on Figure 3 (right panel) indicating that the West Pacific region between  $100^\circ\text{W}$  and  $150^\circ\text{E}$  shows the largest  $\text{CH}_3\text{I}$  abundances. Our model does not take into account terrestrial  $\text{CH}_3\text{I}$  emissions and therefore the very-short lived  $\text{CH}_3\text{I}$  is projected to reach the cold point and enter the stratosphere mostly above the oceans.



**Figure 3.** Comparison between observed and modeled vertical profiles of  $\text{CH}_3\text{I}$  in the upper troposphere and TTL are shown in the left panel. Observations are based on aircraft measurements and model output is averaged over the tropics (blue,  $30^\circ\text{S}$ - $30^\circ\text{N}$ ) and the West Pacific (red,  $100^\circ\text{W}$ - $150^\circ\text{E}$ ,  $20^\circ\text{S}$ - $20^\circ\text{N}$ ) for 2009 and the East Pacific aircraft campaign region (green,  $70^\circ\text{E}$ - $130^\circ\text{E}$ ,  $6^\circ\text{S}$ - $30^\circ\text{N}$ ) for the months of available measurements. The modeled tropical distribution of  $\text{CH}_3\text{I}$  at 17 km for 2009 is shown in the right panel.

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No.	Title
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